

Green Petroleum Refining - Mathematical Models for Optimizing Petroleum Refining Under Emission Constraints

by

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Abstract

Petroleum refining processes provide the daily requirements of energy for the global market. Each refining process produces wastes that have the capacity to harm the environment if not properly disposed of. The treatment of refinery waste is one of the most complex issues faced by refinery managers. Also, the hazardous nature of these wastes makes them rather costly to dispose of for the refineries. In this thesis, system analysis tools are used to design a program that allows for the selection of the optimal control, minimization and treating options for petroleum refinery waste streams. The performance of the developed model is demonstrated via a case study. Optimal mitigation alternatives to meet the emission reduction targets were studied by evaluating their relative impact on the profitable operation of the given facility. It was found that the optimal mitigation steps was to reduce emission precursors by conducting feed switches at the refinery. In all cases, the optimal solution did not include a capital expansion of the emission control facilities and equipment.

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Nomenclature

Parameters

Parameter	Description
$a_{cr,ci,i,p}$	Input-output coefficient for intermediate stream ci from crude cr at plant i
$\beta_{cr,rf,i,p}$	Fuel consumption coefficient of refinery fuel rf from crude cr at plant i by process p
$\gamma_{m,p}$	Assignment from production unit m to process p
$att_{cr,ci,q}$	Intermediate stream attributes ci from crude cr with quality q
$CRcost_{cr}$	Price of crude
$cv_{rf,ci,i}$	Chloric or Btu value of fuel rf by stream ci at plant i
d_{cfr}	Demand for product
$R_{v,l}^+$	Upper limit on each solid waste l from each production unit v
$HG_{v,l}^-$	Lower limit on the cost of switching feed to production unit t v for solid waste l
$HG_{v,l}^+$	Upper limit on the cost of switching feed to production unit t v for solid waste l
DW_{fs}	Solid waste generation factor
$HE_{v,l}^-$	Lower limit on the cost of operating a capture technology to treat effluent production unit t v for solid waste l
$HE_{v,l}^+$	Upper limit on the cost of operating a capture technology to treat effluent production unit t v for solid waste l
$A_{x,n}^+$	Upper limit on each wastewater n from each production unit x
$AG_{x,n}^-$	Lower limit on the cost of switching feed to production unit t x for solid waste n
$AG_{x,n}^+$	Upper limit on the cost of switching feed to production unit t x for solid waste n
$AE_{v,l}^-$	Lower limit on the cost of operating a capture technology to treat effluent production unit t x for wastewater n
$AE_{v,l}^+$	Upper limit on the cost of operating a capture technology to treat effluent production unit t x for wastewater n
Ef_{rf}	Emission factor for air emission

AW_{fs}	Wastewater generation factor
$E_{m,k}^+$	Upper limit on air emissions
$DS_{m,k}^+$	Upper limit on the cost of the fuel switch in air emission
$DS_{m,k}^-$	lower limit on the cost of the fuel switch in air emission
$EOcost_p$	Operating cost of process p
$q_{cr,ci,q}^U$	Upper level of stream with ci quality q a
$q_{cr,ci,q}^L$	Lowe level of stream with ci quality q a
$sg_{ci,cr}$	Specific gravity of intermediate stream ci from crude cr
$maxC_{m,i}$	Maximum production from process unit i

Variables

Variable	Description
$R_{v,l}$	Solid waste flow rate from process unit v and specific pollutant l
$\theta_{m,k}$	Air emission annualized cost of fuel switching on production unit m and pollutant k
$\varphi_{m,k}$	Air emission annualized cost of operating a capture technology on production unit m and pollutant k
$E_{m,k}$	Air emission flow rate from production unit m and pollutant k
$\vartheta_{x,n}$	Annualized cost to reduce process water consumption at production unit x and pollutant n
$\rho_{x,n}$	The annualized cost of operating a capture technology for wastewater treatment at production unit x and pollutant n
$A_{x,n}$	Wastewater flow rate from production unit x and pollutant n
$\sigma_{v,l}$	The annualized cost of feed switch from production unit v and specific pollutant l
$\mu_{v,l}$	annualized cost of operating a capture process for the purpose of limiting solid waste generation from production unit v and specific pollutant l
$z_{cr,p,i}$	Process input flow rate of crude cr to process p at plant i
$S_{cr,i}$	Raw material supply rate of crude cr at plant i
$xf_{cfr,i}$	Mass flow rate of final product cfr at plant i
$xvf_{cfr,i}$	Volumetric flow rate of final product cfr at plant i

Binary Variables

Variable	Description
$Y_{v,l,feedswitch}$	Decision variable representing the selection of feed switching in order to reduce solid waste rate from process unit v and specific pollutant l
$Y_{v,l,capture}$	Decision variable representing the selection of a capture technology in order to reduce solid waste rate from process unit v and specific pollutant l
$Y_{x,n,redconsump}$	Decision variable representing the selection of reduced consumption in order to reduce wastewater rate from production

$Y_{x,n,treat}$	unit x and pollutant n Decision variable representing the selection of treatment technology in order to reduce wastewater rate from production unit x and pollutant n
$Y_{m,k,switch}$	Decision variable representing the selection of fuel switching in order to reduce air emission rate from production unit m and pollutant k
$Y_{m,k,capture}$	Decision variable representing the selection of capture technology in order to reduce air emission rate from production unit m and pollutant k

1.0 Introduction

Petroleum refining is essential in order to provide daily world demand in fuels and chemicals. In 1989, there were 29 refineries producing an average of 248,000 m³ of crude oil daily in Canada.(Losier, 1990).The International Energy Agency forecasts that global demand for energy is expected to increase 35% by 2035 as economies in both developed and emerging countries continue to grow and standards of living improve (IEA Growth 2010 – 2015). Canada is the only OECD (Organization for Economic Co-operation and Development) country with growing oil production, which means more jobs and investment. For example, oil and gas currently provides jobs for 500,000 Canadians, and that number is expected to grow (Canadian Association of Petroleum Producers, 2009).

It is estimated that Oil and gas industry spent \$8.7 billion spends in environmental related issues in the United States (U.S. Oil and Natural Gas Industry's Environmental Expenditures – 1992-2001). Since 1992, API estimates that about \$90 billion (an average of \$9 billion per year) was spent to protect the environment (U.S. Oil and Natural Gas Industry's Environmental Expenditures – 1992-2001).

Crude oil is a continuum of hydrocarbons supplemented with organo-sulfur and organo-nitrogen compounds. The exact composition of crude oil largely depends on its type and its source. The operation of a petroleum refinery starts with the receipt and storage of crude oil at the refinery gate. Several complicated and intensive process are used to produce final products. Separation, conversion, and treating processes are used to

produce various petroleum refinery products. Separation processes such as atmospheric distillation, vacuum distillation, and gas processing are used to separate crude oil into its major components. In turn, conversion processes, such as cracking, visbreaking, polymerization and alkylation, are utilized to produce high-octane gasoline, jet fuel, diesel fuel and other light fractions. This is achieved through the conversion of components such as residual oils and light ends. Last, treating processes stabilize and upgrade petroleum products by separating them from less desirable products and removing unwanted elements (such as sulfur, nitrogen, and oxygen removed by hydrodesulfurization, hydrotreating and chemical sweetening. Other treating processes include desalting and deasphalting - processes used to remove salt, minerals, and water from crude oil prior to refining. Each refining process produces wastes and byproducts that have the capacity to harm the environment if not properly disposed. The hazardous nature of these wastes makes them rather costly to dispose of.

1.1 Solid Waste in Petroleum Refining

The passing of the Resources Conservation Recovery Act (RCRA) in 1976 has forced the treatment of hazardous solid wastes (Environmental Protection Agency, 2006). The RCRA enforces safe handling and disposal of hazardous wastes from municipal and industrial sources. Because of the stringent regulations applied on the hazardous waste producers, increased attention has been focused on different ways to treat and immobilize the wastes. One such industry that is affected by the RCRA is petroleum refining. Large

quantities of wastes are produced from the processing of oil. The treatment and handling of these hazardous wastes is paramount.

The principal contaminants in refinery solid waste discharges are suspended solids in oil, grease, phenols, sulphides and ammonia nitrates. Currently, 81% of Canadian refineries apply secondary or tertiary treatment to their effluent. Sludge from filtration processes may contain volatile compounds such as benzene, as well as phenols and poly-aromatic-hydrocarbons (Government of Canada, 1991). Trace metals, including iron, chromium, lead, mercury, zinc, copper, and vanadium, may also be present. Approximately 30% of these wastes are recycled, 36% are disposed of in landfill sites, 18% are spread on land, 7% are incinerated, 1% are injected into deep wells, and the remainder are disposed of by a variety of other methods.(Government of Canada, 1991)

1.2 Wastewater in Petroleum Refining

Refineries generate contaminated process water, oily runoff, and sewage. Water is used by almost all processing units. Specifically, it is used as “water wash” to pacify acidic gases, stripping water, condensate or caustic. Water is also used as a cooling medium in heat exchangers. The spent water contains harmful chemicals such as phenols and benzenes. Since the passing of the Clean Water Act (Environmental Protection Agency, 1974), reducing contaminant concentration in the effluent discharge has been a focus of the petroleum industry.

Oil refining effluent waste water contains several contaminants that make it unsuitable and unsafe to discharge without treatment. The effluent water must meet the required minimum standards based on established metrics before it is discharged. In 1982, EPA established daily maximum 100 mg/l for Oil and grease content in the effluent from a refinery as well as 100 mg/l for Ammonia as nitrogen and 1 mg/l Total chromium for cooling tower discharge (Environmental Protection Agency, 1974).

The treatment of water in oil refining is therefore complicated by the fact that there are many sources within the refinery which contain different concentration of the contaminants which fall in the above categories. Process waste waters can contain up to 1% dissolved oil, suspended solids from desalters as well as amines (Environmental Protection Agency, 2004). Desalter water can contain dissolved chlorides and nitrates and hard metals such as iron. Process sour water can contain up to 40% H₂S and other polysulfides (Environmental Protection Agency, 2004). Waste water streams are purified and reused to minimize fresh make-up.

1.3 Air Emission in Petroleum Refining

Air emissions are primarily a product of combustion reactions and are mainly generated by process heaters and boilers. The pollutants of major concern are typically SO_x, NO_x, Particulates and Volatile Organic Compounds (VOCs). The emission of nitrogen oxides and sulphur oxides are a major contributor to the global pollution problem. The damaging effect of nitrogen and sulfur oxides on health and environment is substantial. SO_x contributes to acid rain, resulting in deforestation and destruction of coastal and fresh-

water life. NO_x reacts in the atmosphere to form ground-level ozone, bringing about the health-threatening yellowish smog in urban areas.

In Canada, petroleum refining industry accounts for 6.9% of the total SO_x and 3.9% of the total NO_x emission emitted to atmosphere (Government of Canada, 2013). The fraction of Volatile organic compounds emitted by the refining sector accounts for 2.1% of the total emission released to atmosphere. There has been a general reduction in emission over the decades as environmental regulations have been tightened.

1.4 Study Objectives

This study will explore general treatment and disposal practices for refinery solid waste, effluent waste water, and air emissions, with the goal of designing a mathematical model that will optimize the cost of dealing with these wastes for a refinery.

The question this study aims to explore is: *Given an existing refinery, how can the existing controls strategies be supplemented to limit effluent emission from a refinery in order to comply with environmental regulations in the most economic manner.* A difficult problem given that any existing refinery has a number of existing emission sources and each source is emitting and discharging a number of pollutants. Additionally, a number of control strategies might already exist in a refinery, implemented in order to meet certain environmental regulations. Suppose regulations are further tightened as they are currently being done in Ontario (Government of Ontario, 2005), or the refinery is choosing to undergo an expansion of its conversion units, or the feed slate has changed and the refinery is taking in a heavier crude oil containing more sulfur and organo-

nitrogen compounds. Any of these cases will cause an increase in the base load of emissions to the treatment facilities in the refinery. What is required is a detailed and nuanced study of the impact of the change to emissions. For example; the answer is not always to increase capacity of the control facilities. There may be smarter answers that give the refinery a better and improved capability to deal with changes to its operations.

In the development of our approach to solve the proposed problem, the set of all emission and emission sources from a given refinery were collected first. Then, the set of all emission control facility existing at the refinery was collected. Operating cost for each control facility and the capital cost to erect a new facility were collected. Indeed as mentioned before, any change in the refinery emission system will alter either the operating cost of the refinery or the capital expenditure plan for the refinery.

Refiners will have difficult decisions to make in order to meet the impending squeeze in environmental emissions (Government of Ontario, 2005). These decisions can range from a grand expansion of the emission treatment facilities - like the wet gas scrubbers, sulfur recovery plants and water treatment plants - to reducing throughput of emission generating equipment to changing the type of feed the refinery processes. The complexity of the decision and the costs that are associated with making the right decision makes applying mathematical system analysis tools the prudent route going forward. The optimization model will be formulated to deliver the least cost option for the refinery to deal with changing emissions regulatory environment.

2.0 Treatment Approaches for Emissions and Effluents of Petroleum Refining

2.1 Solid Waste

Treating solid wastes from petroleum refining involves thermal, chemical and physical treatment. Each of these technologies offers certain advantages and disadvantages. In petroleum refining, all wastes must be treated in order to achieve the required criteria for disposal.

Thermal treatment unit operates at very high temperatures, usually 800-4000F, to breakdown hazardous chemicals. The final stream could be a less toxic waste aqueous stream which could be further processed to separate the liquid phase from the solid phase.

Some of the industrially available technologies include:

- Rotary kiln oxidation
- Fluidized bed incineration
- Liquid injection incineration

Chemical treatment units operate on the premise of dissolution and concentration gradients. An aqueous waste stream with a known concentration of a specific waste will be contacted with a solvent stream. The solvent is chosen such that waste chemicals in question have a greater affinity to the solvent stream. Therefore, they will be removed from the aqueous waste stream to the solvent stream. The solvent stream is further refined, and might have a market value.

Physical treatment units rely on gravity separation techniques in order to separate the liquid phase from the solid phase in an aqueous phase. Some of these processes are capable of capturing some of the fine solid that are in the mixtures.

2.2 Waste Water

Treatment of refining wastewater is divided in four levels. Primary treatment involves physical treatment, secondary treatments involve the removal of soluble solids, and tertiary involves the biological treatments for final clean up.

Primary Treatment: This stage involves facilities in which suspended solids and free oil can be settled out and the bulk water and oil phases can be separated. Free oil refers to individual oil globules of diameter 150 microns or larger rising to the top of the vessel separator due to the buoyancy force. The solids that will require removal include coke particles from refinery equipment, insoluble salts, and suspended clay particles. The larger of these particles will be removed in the primary gravity separation stage. Smaller particles will remain in the water stream following primary treatment.

The objective of the primary stage is to remove suspended solids and to remove some of the suspended oil in the water stream. The most commonly used technology in industry is the API separators. In a typical API separator, the wastewater stream is first collected in a pre-treatment section to remove gross amount of suspended sludge (Quasim, 1995). A membrane diffusion barrier slowly allows the wastewater to flow down the separator towards the outlet, allowing time to skim the hydrocarbon.

Secondary Treatment: This stage removes dispersed oil and fine solids. Flotation devices are used in which air bubbles are passed through the water stream to increase phase separation force the oil and fine solids to float to the top. The most common technology utilized in industry is the Dissolved Air Flotation (DAF).

This technology has the advantage of high reliability and low cost in addition to good efficiency for the removal of contaminants. In a DAF unit, air bubbles are formed by the reduction in water pressure with pre-saturated air for pressures higher than atmospheric. The re-circulated, pressurized water is forced through needle valves to produce streams of air bubbles of dimensions 30-100 μm in diameter. Oil interacts with the air bubbles, attaches to them, and rises to the surface of the tank where it is removed (Quasim, 1995).

Tertiary Treatment: This involves biological processes in which microbes use the remaining dissolved organics and fine solids as nutrients. In biological treatment, the two types of systems that are most commonly used are the activated sludge process and fixed film systems. The activated sludge process uses a suspended mass of micro-organisms that are constantly supplied with biomass and oxygen. Wastewater flows through the suspension and the microbes treat the water by using the organics as nutrients. After exiting, the suspension goes through a separator in which the organisms are separated from the liquid. Some organisms are wasted as sludge and others are returned to the reactor. The treated supernatant is discharged to the environment (Nemerow & Agardy, 1998).

In fixed film systems, micro-organisms are provided with an attachment surface rather than being suspended. The attachment surface can be granular, plastic, rotating discs,

wood slats or mass transfer packing. There is no need for a separator since the surface area of the packing is designed to ensure an adequate level of biomass. A separator may be supplied to capture the biomass washed from the packing surface. Wastewater may be recycled to control the degree of flushing (Nemerow & Agardy,1998).

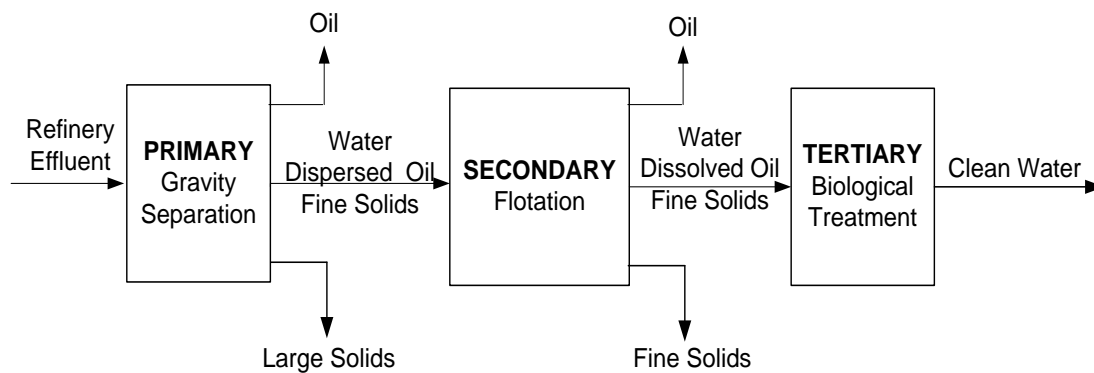


Figure 1: Wastewater flow diagram

2.3 Air Emission

Treatment of air emissions from oil refineries is divided in to two main categories: Source treatment and capture technologies. In source treatment, foulents, such as sulfur in the gas stream is reduced in order to limit the creation of SO_x gases in the effluent. In capture technologies, specific processes have been designed to limit the amount of SO_x and NO_x that is emitted to the environment.

As a primary control strategy, refineries have pursued a path of feed slate optimization to reduce the overall sulfur content in the fuel system. This has been shown to have reduced the amount of SO₂ and NO_x that is generated within the refinery (Parkash, 2003).

Alternatively, other refiners have installed hydroprocessing units to treat sour feeds. This is similar to the approach of reducing the overall feed sulfur to the refinery; both have been shown to lower the overall SO₂ and NO_x generated within the refinery, albeit at the cost of treating an increased number of streams.

Each refinery is unique in the challenges that it may face. The challenges faced by each refinery is complicated by its configuration and operating characteristics. These challenges are determined primarily by the refinery's location, vintage, preferred crude oil slate, market requirements for refined products, and quality specifications for refined products. The predominant fuel used at petroleum refineries is refinery fuel gas (Parkash, 2003). Refinery fuel gas is a non-condensable gas produced by process units such as Crude Distillation unit and the Fluid Catalytic Cracking unit. It is a mixture of gases from C₁ to C₄ including hydrogen sulfide and some organic nitrogen compounds. The fuel gas is typically collected from all process units, treated and routed to process heaters and boilers.

Properties of the fuel system are typically proportional to the overall feed to the refinery. As such, one option of reducing the emission of sulfur oxides and nitrogen oxides is to limit overall sulfur and organic nitrogen content of the crude oil mixture in the refinery. Another option available to refineries is to switch the fuel source from generated refinery fuel gas to purchased cleaner nature gas from a local utility provider. In order to pursue this option a refinery must have a customer for its produced gases.

Secondary levels of control are geared towards treatment. The two types of treatment are source treatment and effluent treatment. In source treatment, the objective is to reduce or

eliminate precursors such as sulfur and organic nitrogen before process units generate gas streams. Any sulfur in the refiner fuel system is a result of sulfur that is present in the feed, thereby treating the feed sulfur streams will reduce the amount of sulfur in the refinery fuel system. The most widely used technology to treat sulfur and nitrogen in hydrocarbon streams is Hydrotreating. Catalytic hydrotreating removes sulfur and organic nitrogen by using high hydrogen partial pressure, specially designed catalyst and moderately high temperature. The effluent streams usually contain less than 90% of the feed sulfur (Jones & Pujadó, 2006).

In effluent treatment, gas streams are usually treated for impurities prior to them being sent to refinery fuel system. In Wet Gas Scrubbing, steam mixed with an alkali reagent is used to react with SO_x and NO_x-containing process gases. In the process, up to 90% reduction in contaminants can be achieved (Jones & Pujadó, 2006).

3.0 Literature Review

System analysis and process optimization have been a mainstay in the petroleum industry for many years. It has been applied to production planning, resource alignment and process execution (M. W. Padberg; 1999). The objective has always been to maximize profits and minimize expenditure (M. W. Padberg; 1999). More recently, researchers have been applying similar techniques to the problem of environmental emission generated at the facility level (Jones & Pujadó, 2006). Due to the complex number of emission sources each generating multiple types of emissions and the inherent techno-economic interconnectivity of petroleum refining, there have been several approaches to tackle the problem of minimizing environmental emissions from petroleum refining (Famim et al. 2009). Each approach has its benefits and drawbacks. The following section further explores the research that has been done and the area remaining to be investigated.

3.1 Generalized Approaches

Numerous authors have attempted over the years to tackle the problem of air pollution. Flagan and Seinfeld (1988) divided the problem of air pollution abatement into two categories: long-term control and short-term control. Long-term control includes urban planning, rescheduling of activities, and programmed reduction in the quality of pollutants emitted. Short-term control strategy, on the other hand, involves rescheduling of activities and immediate reduction in emissions.

Guldmann and Shefer (1980) attempted to classify emission control approaches as simulation/input-output approaches, and cost-effective optimization approaches. These

approaches can further be subdivided to emission-oriented optimization models, and ambient air quality oriented optimization models. These models comprise static and dynamic approaches. Based on the goal of meeting air pollution abatement with air quality standards as the goal.

Pirrone and Batterman (1995) developed cost curves that used one or several control strategies to achieve a range of concentration reductions. Their ultimate goal was to find out the preferred strategies at various mitigation levels. The results indicate preferred and optimal strategies at various mitigation levels. This approach did not attempt to select a control strategy under uncertainty nor did it attempt to solve the selection problem.

Wastewater research from industrial plants in literature has dealt with the issue of minimizing wastewater generation in water using processes separately from the design of effluent treatment systems. Wang and Smith (1994) have proposed water reuse, regeneration-reuse, and regeneration-recycling as an approach for wastewater minimization. In this research, they have also proposed a methodology for designing effluent treatment systems where wastewater is treated in a distributed manner. In this ‘distributed method’, the effluent streams are treated separately instead of combining them into a single stream prior to treatment, reduces the treatment cost since the capital cost and operating cost of a treatment operation are directly proportional to the water flowrate through the treatment.

Although not much work has been done in mathematical optimizing models of solid waste collection in the refining industry, much work has been done in exploring solid

waste at the municipal level. For example, Eisenstein and Iyer (1997) investigate the scheduling of garbage trucks in the city of Chicago and developed a flexible routing strategy with regard to the number of visits to the waste disposal site. The study approach was to use Markov decision process. The approach resulted in reducing the amount of trucks utilized in the city.

Haq et al. (1997) conducted a cost-benefit analysis of pollution control equipment installed to contain dust emissions in the Indian Cement Industry. Plants of a certain level of production were assessed. Their analysis was based on a selection of the control equipment, which complies with the emission regulations, at the lowest cost. The study found that most plants pursued a time-targeted schedule to install the required pollution control equipment. This minimized the risk of capital expenditure for the facilities.

The Graphical Method has the advantage of being simple to construct. However, it is limited in its capacity to solve large and complex problems. The Graphical Method calculates the objective function value at all vertices of the feasible region. Problems with high combinatorial complexity may take time to solve. The solution obtained is usually not a global optimum.

3.2 System Analysis Approaches

System analysis has been proven to be an effective tool for economic evaluation of environmental problems. Many researchers have explored the use of various techniques. Systems analysis, such as linear and integer programming, has been applied to environmental economic evaluation.

Kohn (1968) proposed a mathematical model to determine the appropriate air pollution control strategy for a given air-shed. The approach used linear programming model. The goal of the study was to select the best method of mitigating air quality issues at the least possible cost. The model was relatively simple; it emphasized only the percent use of a control strategy and not on the selection of pollution control.

Schweizer (1974) developed a method for the optimal mix of high and low sulfur fuels for power plants so that environmental criteria are met. The fuel mix target was determined so that environmental limits are met and plant operating schedules are fully maintained. The problem is formulated in a "minimum energy with penalty function" format. Well-known optimal control theory methods are applied to obtain the solution. Allowing for variable feeds to meet emission limits presents a unique perspective at emission optimization problem but similar to previous approaches, it does not attempt to solve the selection problem.

Lou et al. (1995) used linear programming analysis for the optimal arrangement of pollution control equipment among individual workshops within a plant under the regulation of total emission control. Results show that the total annual cost of a plant increases with decreasing total emission standards. Under a given total emission standard, sensitivity analysis suggests that the larger the allowable variation range of unit cost of a control equipment, the smaller the risk for that workshop. In their approach, the costs, efficiencies, emission factors, types and characteristics of control equipment were examined under various total emission standards.

Janssens (1993) describes a mathematical model to determine the optimal vehicle fleet size for collecting waste oil in Antwerp in Belgium. The model consists of demand estimation and a collection model that estimates the number of routes and required travel times. To conclude their study, suggestions are made to speed the problem solving and limit the storage use in the computer.

Chang, Lu, and Wei (1997) describe a mixed-integer programming model for routing and scheduling of solid waste collection trucks. The model is integrated with a GIS environment and an interactive approach. They also present a case study in Taiwan. Their unique approach allows decision-makers to assess and analyze multiple routing at once. Smith Korfmacher (1997), on the other hand, presents a case study on designing solid waste collection for urban areas in South Africa. They discuss a number of strategies for arranging the collection operations.

Bommisetty, Dessouky, and Jacobs (1998) consider the problem of collecting recyclable materials in a large university campus. The problem was modeled as a periodic VRP, and a heuristic two-phase solution method is suggested.

Tung and Pinnoi (2000) address the waste collection activities in Hanoi, Vietnam. The underlying real-life vehicle routing and scheduling problem is formulated as a mixed integer program, and a hybrid of standard VRP construction and improvement heuristics is proposed for its solution. Mourão (2000) uses a route first-cluster second approach where a giant tour is generated first, and then decomposed with a lower-bounding method into a set of routes that are feasible with regard to the vehicle capacity. Bodin, Mingozzi, Baldacci, and Ball (2000) study rollon–rolloff VRP faced by a sanitation company. In

the rollon–rolloff VRP, tractors move large trailers between locations and a disposal facility, one at a time. The authors present a mathematical programming model and four heuristic algorithms for the problem. The same problem is studied earlier in De Meulemeester et al. (1997).

Shih and Chang (2001) develop a two-phase approach for routing and scheduling the collection of infectious medical waste from a set of hospitals. In the first phase, a standard VRP is solved by a dynamic programming method while the second phase uses a mixed integer programming method to assign routes to particular days of the week.

Feng et al. (2001) have proposed an internal structure to tackle water consumption as an ultimate means of reducing waste water generation. Alva-Argaez et al. (1998) have used a mathematical programming approach to optimize a superstructure, which includes possibilities for water treatment and reuse. In their solution approach, they present a mixed integer non-linear model, which is decomposed into a sequence of mixed integer linear problems to approximate the optimal solution.

Golden, Assad, and Wasil (2001) give a short review and analysis of real-life applications. Baptista, Oliveira, and Zúquete (2002) present a case study on collection of recycling paper in Portugal. The problem is modeled as periodic VRP and a heuristic approach is presented that consists of initial assignment of collection tasks to days, and interchange moves to improve the solution. Minciardi, Paolucci, and Trasforini (2003) describe heuristic strategies to plan routing and scheduling of vehicles for very large-scale solid waste collection that takes place at a district level instead of municipal level. A case study at Geneva, Italy is presented. Teixeira, Antunes, and de Sousa (2004) study

the planning of real-life vehicle routes for the collection of different types of urban recyclable waste in Portugal. Heuristic techniques were developed to define the geographic collection zones - waste types to be collected on each day and vehicle routes. Koushki, Al-Duaij, and Al-Ghimlas (2004) present a case study to evaluate the efficiency of municipal solid waste collection in Kuwait. Several indicators to measure the effectiveness are proposed and discussed, and a comparative analysis of the collection costs is reported.

Amponsah and Salhi (2004) describe a constructive look-ahead heuristic with tailored improvement mechanisms that are specifically designed for collecting garbage in developing countries. Aringhieri, Bruglieri, Malucelli, and Nonato (2004) study the real-life collection and disposal of special waste such as glass, metal and food. The special waste is collected from containers at collection centers instead of each household. Thus, the problem can be modeled as the rollon–rolloff VRP. Standard heuristic construction and improvement procedures as well as lower bounding procedures are presented.

A superstructure given by Wang and Smith (1994) for distributed water treatment network was optimized by Galan and Grossmann (1998). The given heuristic was a mathematical programming procedure for the optimal design of a distributed wastewater treatment network.

Lee and Grossmann (2003) further optimized the work done by Galan and Grossmann by suggesting a global optimization algorithm for nonconvex Generalized Disjunctive Programming (GDP) problem. The proposed algorithm exploits the convex hull

relaxation for discrete search, and the fact that the spatial branch and bound is restricted to fixed discrete variables in order to predict tight lower bounds.

3.3 The Selection Problem

Even though linear programming models are simpler to solve than integer programs, the main drawback of these models is that they determine the percent utilization of a control option only. These models, therefore, are not an effective tool to determine binary problems such as the selection of a control strategy.

Kemner (1979) developed a computer model for coking facilities, which allows the user to determine the optimum mix of pollution control devices to achieve a specified reduction in pollutant emission at the minimum annualized or capital cost. The selected approach, an integer based linear programming model, was applied to a coke plant and was solved by trial and error using plots of the control cost for various desired reductions.

Holnicki (1994) presented a similar model for implementing a pollution control strategy at a regional scale. The model was solved using a heuristic technique that systematically tries to determine a good (sub-optimal) solution to the control selection problem.

Elkamel et al., 1998 developed a mathematical model for emission reductions in emissions during oil production operations. In their approach, a mixed-integer nonlinear programming model is proposed for the production planning of refinery processes to achieve maximum operational profit while reducing CO₂ emissions.

Elkamel and Al-Qahtani, 2007 proposed a model based on State Equipment Network (SEN) representation for refining process. The problem was formulated as a mixed

integer linear program (MILP). Binary variables are used for selecting the optimal pollutant control strategies. The resultant was program was applied to air pollution mitigation at a plant.

Although refining air emission has been modeled well by Elkamel and Al-Qahtani, there is an opportunity to supplement their work with predictive wastewater and solids waste emission optimization models for petroleum refining. In this study, the complexity of the refining planning model is reduce by removing the global intergrading of crude oil and products. Emission factors are developed based on simulation case studies. The objective is to optimize the cost effectiveness of the modeled refinery under different emission constraints. By doing so, a refinery operator may be able to predict emissions based on a given operating strategy. The tools can also be used by a refinery planner to plan an annual operating strategy that stays within a given operating envelope.

4.0 Predictive Model Formulation

The model developed in this research is based on a typical crude oil refinery as shown in Figure 2. The objective of the model is to select the best option for generating products while minimizing emissions. We will attempt to develop a model that has two distinct sections: (1) A yield and an emission predictive section. In the section, the model will be able to predict the yields of each process unit as the operating conditions are varied. The model will be designed such that it is responsive to variation of operating modes and feed qualities this will be reflected in yield shifts and product quality changes. (2) A process optimization section. In this section, the model will be designed to select the best of several emission mitigation options while still meeting the product yield requirements.

To meet the objective of this research, first a method to predict the product yields and emissions generated as a byproduct from each process unit as a function of feed characteristic and process unit rates must be created. As such a yield and emission coefficients for each process unit must be created. These factors are a function of process unit operating variables and feed quality. Using factors to predict outcomes of the process unit in an attempt to simplify the thermodynamic implication and feed quality precursors that impact both the yield and emission that are generated as part of operating a process unit.

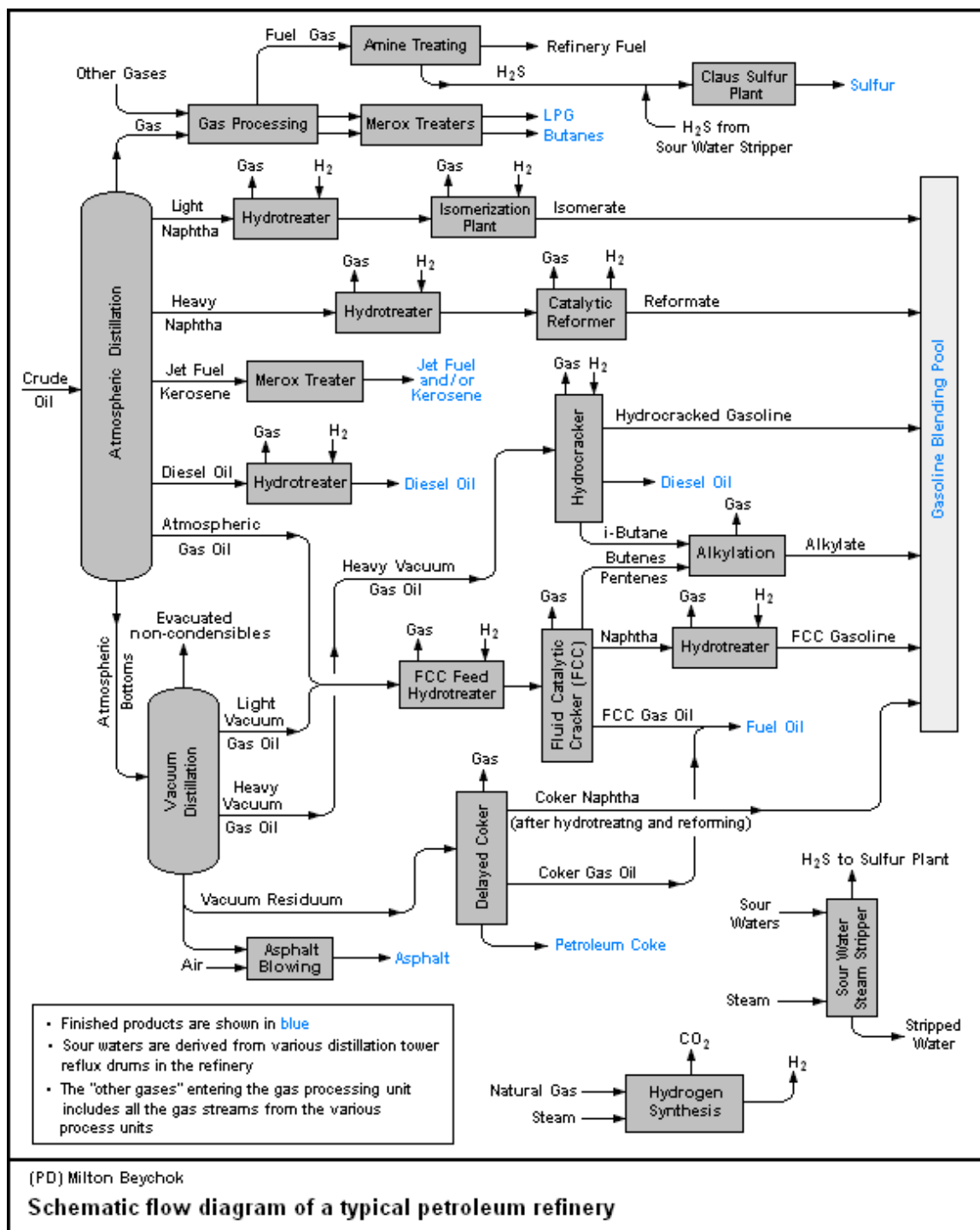


Figure 2: Typical Refinery Flow Diagram

4.1 Emission and yield Coefficient

The emission and yield coefficient were obtained by designing and implementing a rigorous process heat and material balance model for each unit using commercially available ASPEN HYSIS software. Each process unit was initially subjected to varying operating conditions at constant feed characterizations. This allowed for generating yield coefficients as a function of process condition followed by conducting similar cases in which operating conditions were fixed and feed characteristics were varied.

Emission coefficients from operating process units are slightly more complex than yield coefficient in that emissions are a product of the yields in the process. Material balancing needs to be taken into account while conducting process conversion (i.e reforming and cat cracking). This is shown schematically in the following figure:

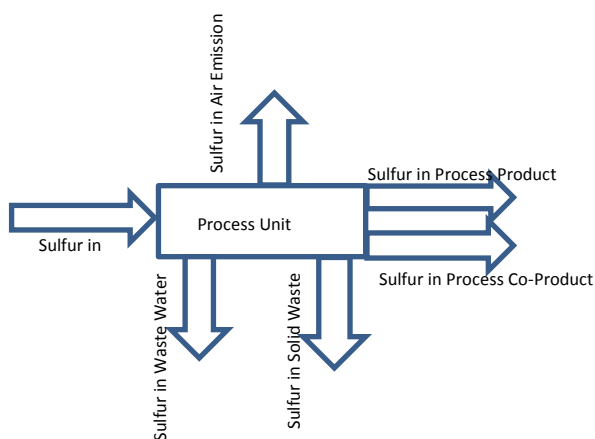


Figure 3: Emission Balance

4.1.1 Crude Oil Properties and Impact on Refining Product Properties and Emission Generation

Crude oil is the basic raw material into a petroleum refinery. The chemical compositions of crude oils are uniform even though their physical characteristics vary widely (Kraemer & Calkin, 1925). Approximately 85% of the elemental composition by weight of crude oil is Carbon (Kraemer & Smith, 1924). Hydrogen makes up about 14% with the rest of the crude oil being composed of Nitrogen, Sulfur (Kraemer & Smith, 1924). There are organo-metals such as Iron and Lead that maybe found in some crude oils (Lane & Garton, 1937),

Crude oil properties can further be described as the nature of the carbon-to-carbon base connection. This carbon base connection can be classified as paraffin base, naphthene base, asphalt base, or mixed base (Lane & Garton, 1937). There are some crude oils in the Far East which have up to 80% aromatic content, and these are known as aromatic-base oils. The U.S. Bureau of Mines has developed a system which classifies the crude according to two key fractions obtained in distillation: No. 1 from 482 to 527°F at atmospheric pressure and No. 2 from 527- 572°F at 40 mmHg pressure (Lane & Garton, 1937).

API gravity and sulfur content have had the greatest influence on the value of crude oil, although nitrogen and metals contents are increasing in importance (Manning et al, 1995). The higher API crudes are referred to as light or lower density crudes while the lower API crudes are referred to as heavy crudes. The sulfur content is expressed as percent sulfur by weight and varies from less than 0.1% to greater than 5% (Manning et

al, 1995). Typically, in refining industry, hydrotreating and hydrodesulfurization are the techniques used to remove sulfur.

The term “Sour” crude oil has been generally used to refer to higher sulfur content crude oils (Manning et al, 1995). Sour crude oils typically require more extensive processing than those with lower sulfur content (Drews, 1998). There is no sharp dividing line between sour and sweet crudes but 0.5% sulfur content is frequently used as the criterion.

Nitrogen is another contaminant that is found readily in crude oil. High nitrogen content is undesirable in crude oils because organic nitrogen compounds are poisons to hydrotreating and reforming catalysts (Drews, 1998). Crudes containing nitrogen in amounts above 0.25% by weight require special processing such as hydrotreating and saturating the organo-metal bonds to remove the nitrogen (Drews, 1998).

Metals, even heavier types, can be found in some source rocks that produce hydrocarbon oils. Even at low concentration, metals can have tremendous impact on refining processes. Small quantities of some of these metals (nickel, vanadium, and copper) can severely affect the activities of catalysts and result in a lower- value product distribution (Drews, 1998).

4.1.2 Emission and Yield Coefficients for Pipestill Unit

The crude distillation unit also known as the crude pipestill is the first major process unit in petroleum refining. This process is used to separate crude oil into different fractions based on distillation and boiling point. In the pipestill, there are three major process

activities that ultimately yield the separation of crude oil into the different fractions: Desalting, Atmospheric Distillation and Vacuum Distillation.

Salts in crude oil are present in the form of dissolved or suspended crystalline salts in water emulsified with the crude oil. If the salt content of the crude oil is high then the crude requires desalting to minimize fouling and corrosion caused by salt deposition (Fahim et al, 2009). Fouling is primarily found on heat transfer surfaces such as heat exchangers and furnaces (Fahim et al, 2009). Acids formed by decomposition of the chloride salts are normally a concern in fractionation tower overhead systems (Fahim et al, 2009).

The principle of Desalting is to wash the salt from the crude oil with water by intimately mixing the oil with wash water. A secondary but important function of the desalting process is the removal of suspended solids from the crude oil. These are usually very fine sand, clay, and soil particles; iron oxide and iron sulfide particles from pipelines, tanks, or tankers; and other contaminants picked up in transit or production (Fahim et al, 2009). Electrostatic plates within the desalter are used to separate oil and water droplets (Fahim et al, 2009). The operation of a desalter can be very challenging due to changing process variables. Operating difficulties can occur in obtaining efficient and economical water/oil mixing and water-wetting of suspended solids in the mixing area (Gary & Handwerk, 2001). In the separation phase, challenges can be encountered in the separation of the wash water from the oil (Parkash, 2003). Crude oil such as pH, gravity, and viscosity have an effect on the separation ease and efficiency (Wauquiere, 2000).

Heat source for the pipestill is typically process heaters which operate to meet the required flash zone temperatures. Furnace outlet temperatures are also a function of the vapor fraction as well as coking characteristics (Gary & Handwerk, 2001). High tube velocities and steam addition minimize coke formation. Furnace outlet temperatures in the range of 730°F to 850°F are generally used (Gary & Handwerk, 2001).

The vacuum pipestill is used to separate the heavier portion of the crude oil at lower temperatures. This avoids thermal cracking, coke formation, and dry gas production at higher temperatures. Vacuum Distillation is carried out with absolute pressures in the tower flash zone area of 25 mmHg to 40 mmHg. The lower operating pressures cause significant increases in the volume of vapor per barrel vaporized. As a result, the vacuum distillation columns are much larger in diameter than atmospheric towers (Wauquire, 2000).

The product yield as a function of flash zone operating condition is shown in Figure 4. The graphs show a linear response to separation and production of lighter naphtha products as temperature rises. This occurs due to an increase in the partial fraction of vapour in the feed increasing as the flash zone temperatures increases. The same response can be observed as the operating pressure is decreased. This is shown in Figure 5.

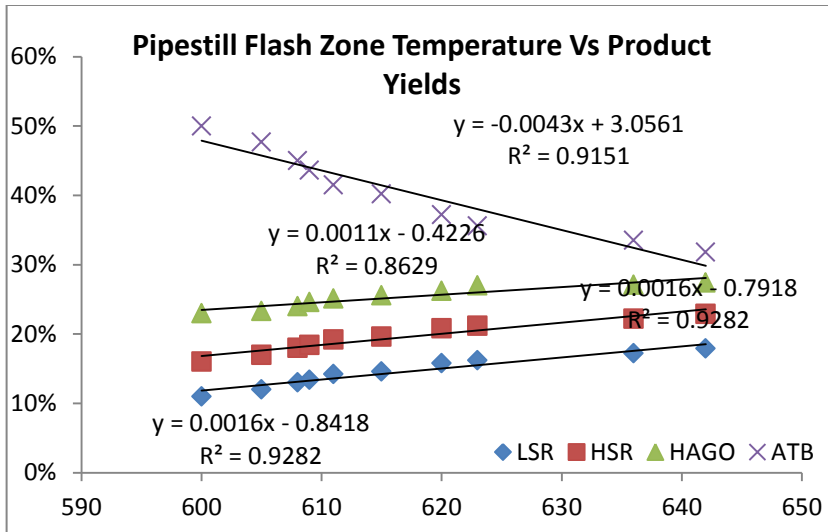


Figure 4: Pipestill Flash Zone Temperature vs Product Yields

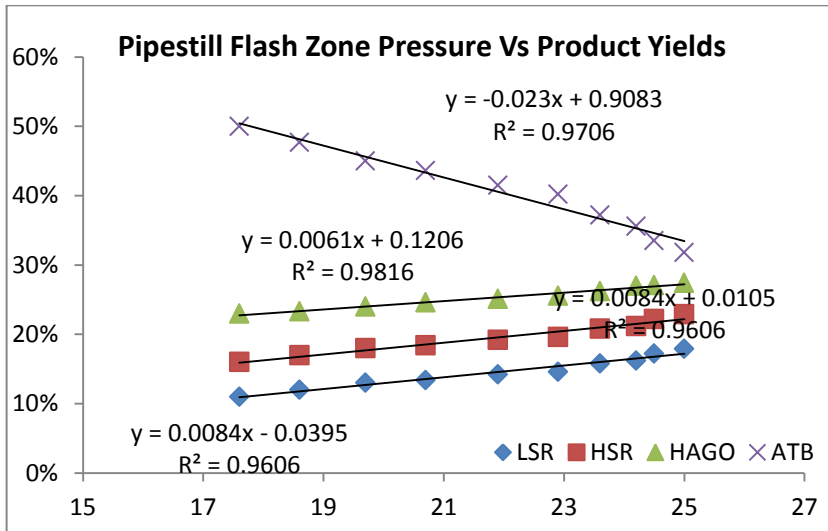


Figure 5: Pipestill Flash Zone Pressure vs Product Yields

The emission generation of the pipestill as a function of rate is shown in Figure 6. There is a linear and increasing response of waste generation as the pipestill rate is increased. This is primarily due to increased load being placed on the process heaters and steam side strippers to provide separation. As the rate is increased, mass hydrocarbon rate increases through the process heaters and the side strippers. In order to achieve constant material

yields, stripping steam and heat duty are increased to meet the desired objective. This has the effect of increasing the Sour Water production, H₂ and SO₂ production.

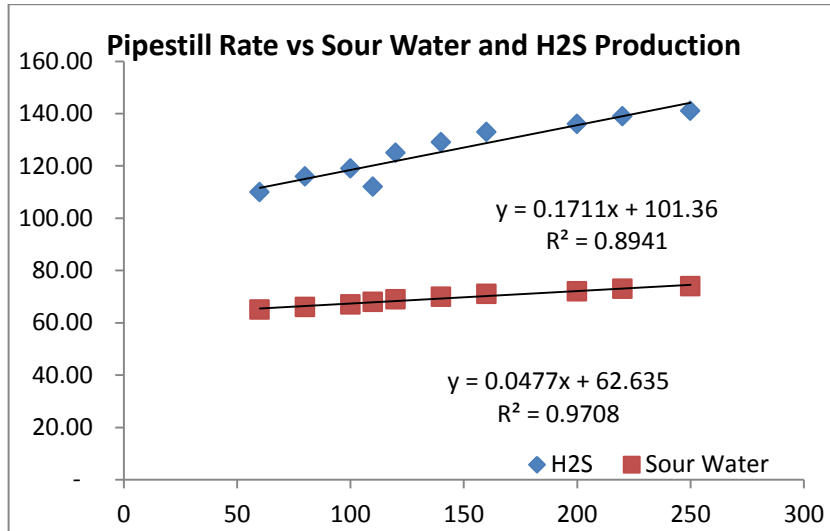


Figure 6: Pipestill Rate vs Sour Water and H₂S Production

The crude pipestills are the first major processing units in the refinery. They are simple in its objective; utilize heat and partial pressure variation to achieve separation of hydrocarbon based on boiling points. The product yields have a linear response to both operating temperature and operating pressure while the air and water emissions are a function of mass rate of the unit.

4.1.3 Fluid Catalytic Cracking Unit

Catalytic cracking is the most important upgrading and conversion unit in the refinery. It is used to upgrade heavy atmospheric and vacuum gas oils into lighter components which are used in gasoline and diesel blending. Originally, cracking was accomplished thermally. The catalytic process has almost completely replaced thermal cracking

because more gasoline having a higher octane and less heavy fuel oils and light gases are produced (Parkash, 2003).

There are two primary vessels in the Fluid cracking units. The Regenerator is used to regenerate catalyst (Parkash, 2003). Coke which is a byproduct of the reaction process is laid down on the catalyst in the reactor (Sadeghbeigi, 2000). Coke is considered to be temporary poisons on the catalyst (Sadeghbeigi, 2000). The reactor vessel is used to contact catalyst with the hydrocarbon feed allowing for the cracking reaction to take place and then disengage and separate the catalyst from the hydrocarbon (Sadeghbeigi, 2000). The cracking reaction is endothermic and the regeneration reaction exothermic (Magee & Mitchel, 1993). Average reactor temperatures are in the range 900°F to 1000°F, oil feed temperatures ranging from 500°F to 800°F, and regenerator exit temperatures for catalyst ranging from 1200°F to 1500°F (Sadeghbeigi, 2000).

Gas oil is heated prior to contacting the catalyst in the reactor riser system (Sadeghbeigi, 2000). The catalyst progressively deactivates with coke as the reaction proceeds (Sadeghbeigi, 2000). The reactor cyclone systems are used to mechanically separate the catalyst from the reactor vapors. Steam is used in the reactor stripping section to remove remaining hydrocarbon from the catalyst prior to entering the regenerator vessel. The hydrocarbon vapors are carried out to the separation section of the FCC. The spent catalyst flows into the regenerator and is reactivated by burning off the coke deposits with air (Sadeghbeigi, 2000).

Temperatures in the regenerator vessel are operated to balance burning and removing the carbon off the catalyst avoiding permanent destruction and deactivation of the catalyst (Parkash, 2003). This is accomplished by controlling the air flow to give a desired CO/CO ratio in the exit flue gases or the desired temperature in the regenerator (Magee & Mitchel, 1993). The flue gas and catalyst are separated by cyclone separators and electrostatic precipitators.

The product yields of the Fluid Catalytic Cracking unit as a function of reactor temperature is shown in Figure 7 and Figure 8. The yield coefficient for the gasoline component at the FCC (430°F -) show a strong increasing yield relationship with increasing reactor temperature up to 992°F. Above this temperature, “over-cracking” is observed. This is the point where an increase in the production of propylene (C3-) and butylene (C4-) components at the expense of gasoline components (430°F -) is observed.

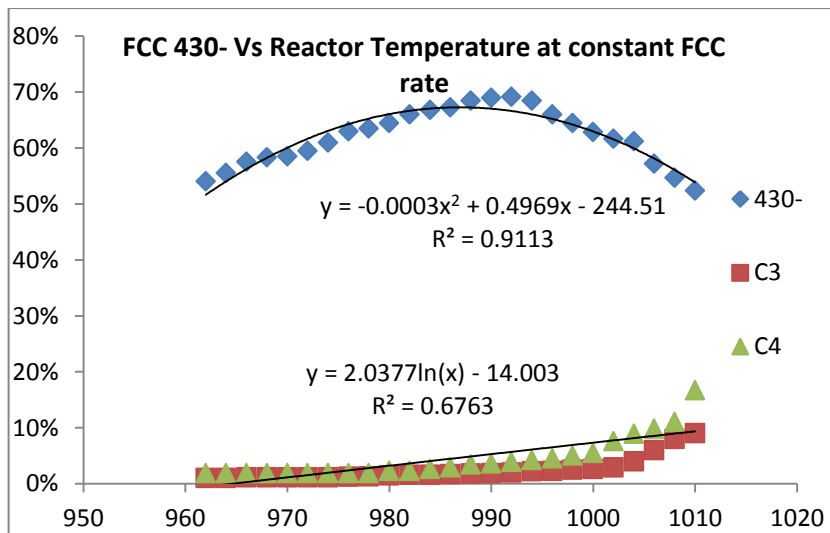


Figure 7: FCC 430- vs Reactor Temperature at Constant FCC Rate

The diesel fraction (430°F -650°F) yield shows a linear positive and increasing response to reactor temperature up to 988°F, after which we observe a decline in the yield of diesel at the expense of incremental yield in gasoline. At this reactor temperature, we observe the end of what the industry terms to be ‘end to bottoms upgrading’.

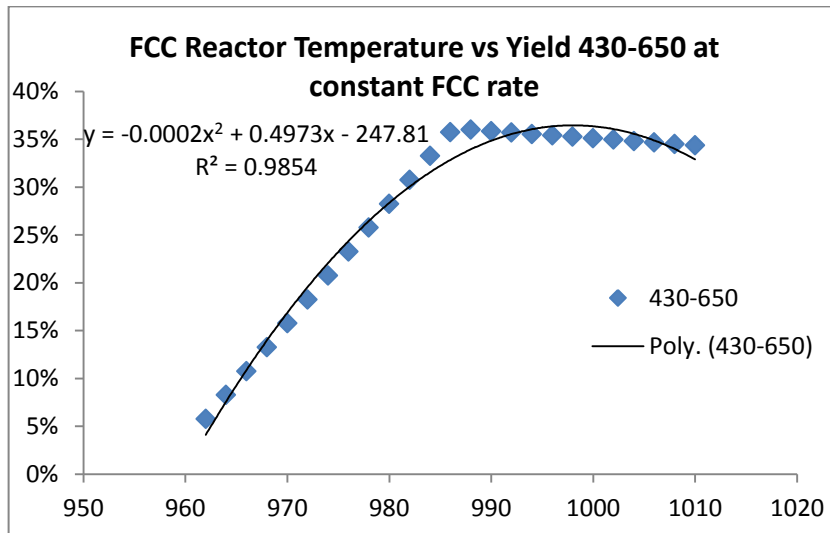


Figure 8: FCC Reactor Temperature vs Yield 430-650 at Constant FCC Rate

The yield coefficient as a function process rate is shown in Figure 9. Not surprisingly, a flat and non-responsive line for each product fraction is observed. This is due to the fact that for the process, yield does not change due to the process rate being within the design rates for the equipment. In other words, we do not see a significant change in process rate to cause a reduction in residence thereby impacting the yield from the unit. A relative change in production of sour water and effluent process gas as a function of process rate is observed. This is shown the following graph:

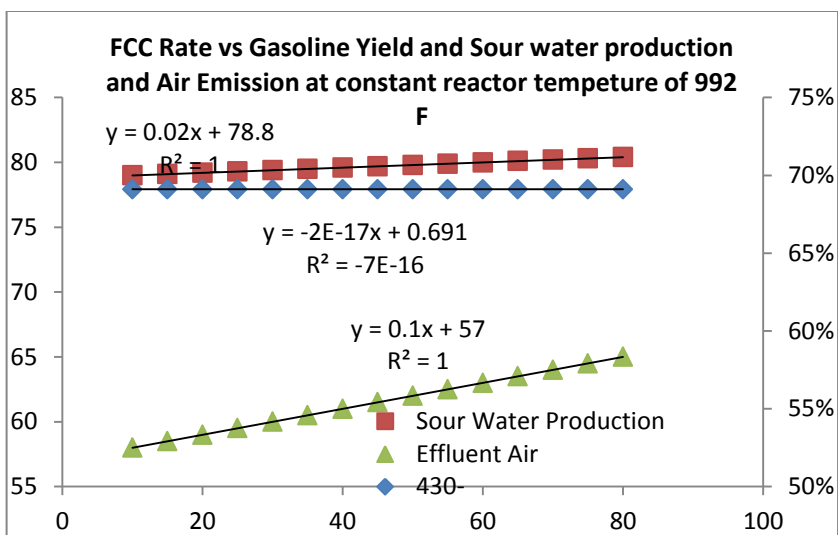


Figure 9: FCC Rate vs Gasoline Yield and Sour Water production and Air Emission at Constant Reactor Temperature of 992 F

The cases which were modeled to determine the emission coefficient for feed sulfur and nitrogen show a linear positive response to emission in the effluent stream. These emission coefficients were developed at a constant reactor temperature of 992°F. This was repeated at each reactor and feed rate combination to develop a matrix for each feed rate and reactor combination.

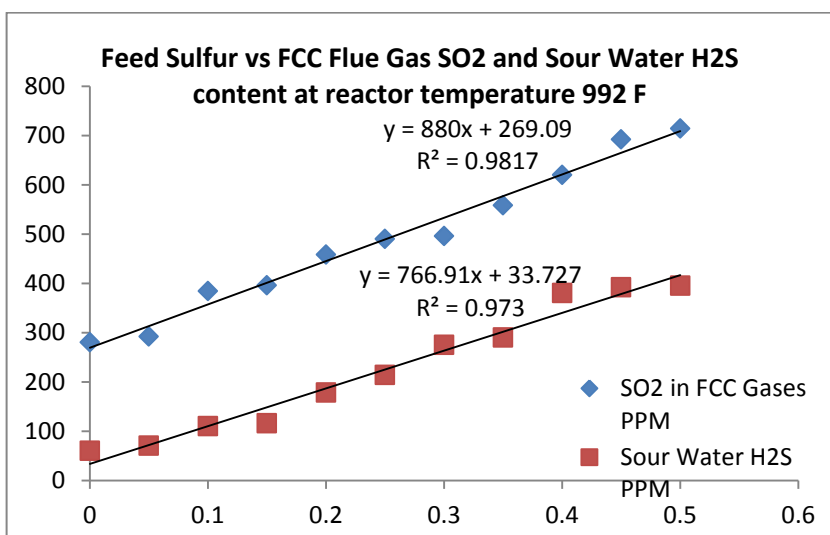


Figure 10: Feed Sulfur vs FCC Flue Gas SO2 and Sour Water H2S Content at Reactor Temperature 992 F

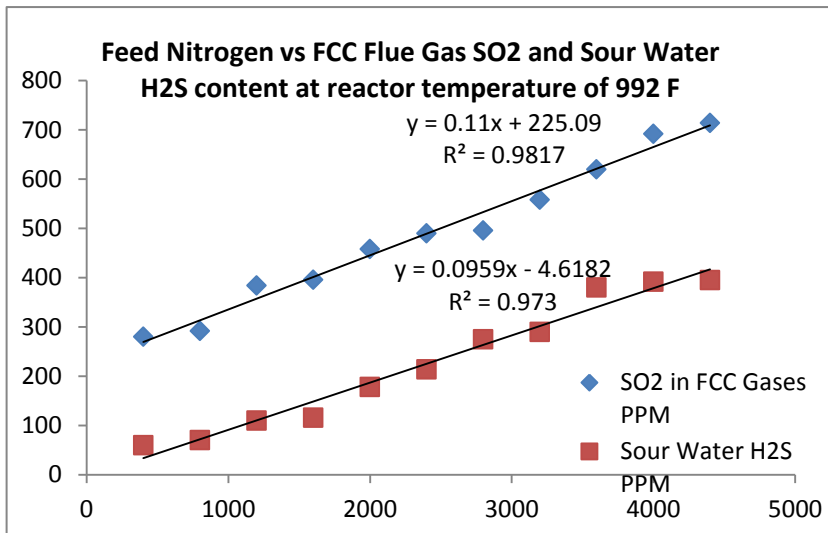


Figure 11: Feed Nitrogen vs FCC Flue Gas SO₂ and Sour Water H₂S Content at Reactor Temperature of 992 F

The emission coefficient as a function of unit feed rate is shown in Figure 12. As expected, there is a strong linear relationship between SO₂ and NO_x production and unit feed rate. Similar to other emission factor generation, this is at a constant reactor temperature. Therefore, this was repeated for all possible reactor temperatures in order to develop a matrix of emission factors.

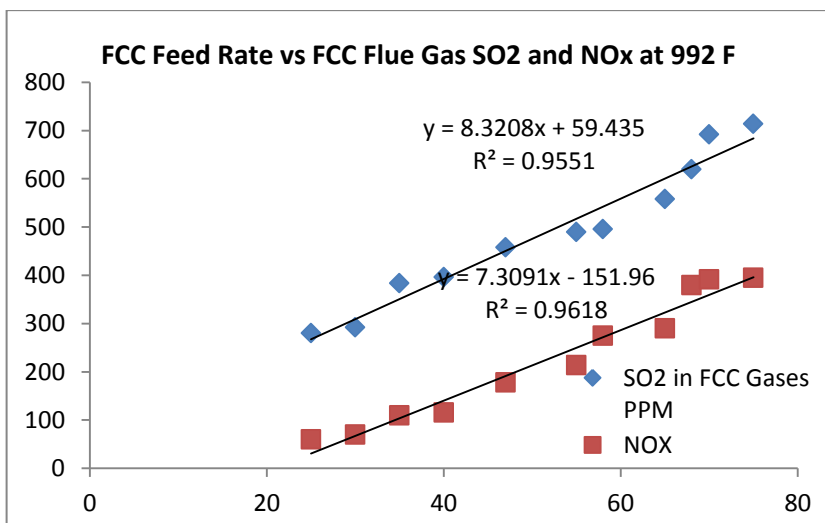


Figure 12: FCC Feed Rate vs FCC Flue Gas SO₂ and NO_x at 992 F

Catalytic cracking is one of the main conversion platforms in petroleum refining. Catalytic cracking takes relatively low value gas oil feed from the pipestills and is able to convert it to high value finished materials such as gasoline and diesel. The yield for the gasoline component at the FCC (430°F) has a strong increasing yield relationship with increasing reactor temperature up to a given temperature. Beyond this temperature we observe an increase in the production of propylene (C3-) and butylene (C4-) components at the expense of gasoline components (430-). Consequently, the diesel fraction (430-650) yield shows a linear positive and increasing response to reactor temperature up to a given temperature after which we observe a decline in the yield of diesel at the expense of incremental yield in gasoline. The SO₂ and NO_x generated at the FCC have been shown to be modeled as a function of feed rate, feed Sulfur and Nitrogen content.

4.1.4 Reforming Unit

Catalytic reforming is used to convert low octane hydrocarbon to high octane gasoline components. This is accomplished by reconstructing the molecule without changing the boiling range of the entire stream (Antos & Aitani, 2004). Other valuable byproducts include hydrogen and Cracked light gases. Major types of reactions which occur during reforming processes:

- Dehydrogenation of naphthanes to aromatics
- Dehydrocyclization of paffins to aromatics
- Isomerization
- Hydrocracking

Naphtha from different sources varies greatly in its tendency to easily and efficiently reform (Antos & Aitani, 2004). Straight run naphtha are generally easier to reform and generally produce higher hydrogen yield (Parkash, 2003). Non-straight-run naphthas, for example FCC Naptha, can be processed in a CRU but only after severe hydrotreatment involving di-olefin saturation (Antos & Aitani, 2004) . Their higher endpoint and higher paraffin content result in a higher coke laydown and lower hydrogen yield (Antos & Aitani, 2004).

The basic reaction of reforming is the conversion of naphtha to aromatics. Paraffins are the most difficult compounds to convert. A rich naphtha with lower paraffin and higher naphthene content makes the operation much easier and more efficient (Antos & Aitani, 2004). The types of naphtha used as feed to the CRU can impact the operation of the unit, activity of the catalyst and product properties (Antos & Aitani, 2004).

There are two different strategies to operate a CRU in refining. When catalytic reforming is used mainly for BTX and chemical precursor production, a C6-C8 cut rich in C6 is usually employed (Antos & Aitani, 2004). For production of a high-octane gasoline pool component, a C7-C9 cut is the preferred choice (Gary, 2001). In all cases, feedstocks to catalytic reforming processes are usually hydrotreated first to remove sulfur, nitrogen, and metallic contaminants (Antos & Aitani, 2004).

The yield coefficient for the reforming unit products as a function of the reactor temperature shows a strong increasing relationship at a constant feed rate. We also observe the octane of the product increasing with reactor temperature. This is shown in

Figure 13.

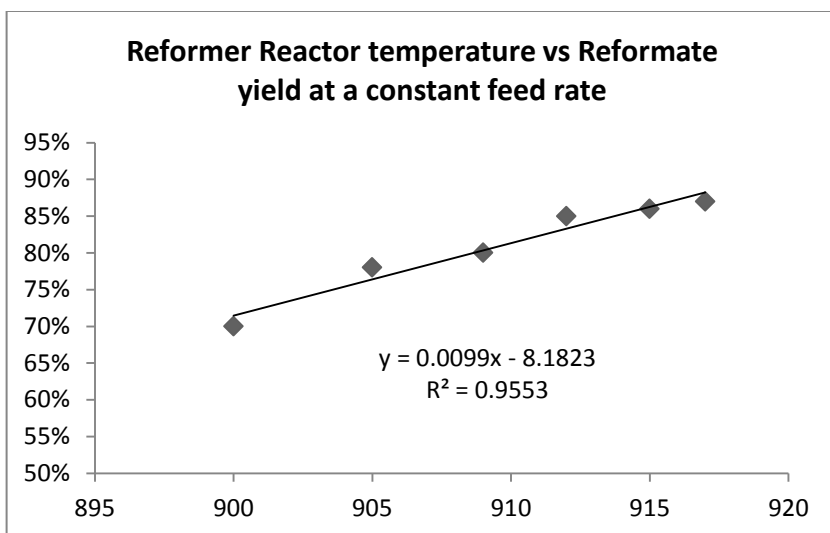


Figure 13: Reformer Reactor Temperature vs Reformate Yield at a Constant Feed Rate

The yield coefficient for feed sulfur is shown in Figure 14 and Figure 15. Sulfur is a temporary poison to the catalyst and has a negative impact on the reformate yield. These cases were developed at a constant reactor temperature. This was repeated for multiple reactor temperatures to develop the matrix of coefficients. The relationship changes with different reactor temperatures. This due to the complex factors of coke laydown and sulfur poisoning. At higher temperatures, hydrocarbon coke laydown on the catalyst increases due to sulfur compounds poisoning the active site of the catalyst.

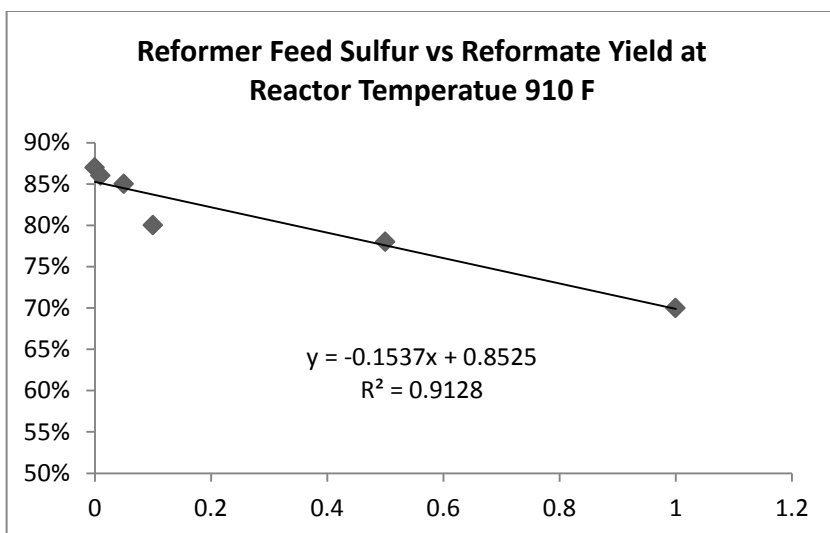


Figure 14: Reformer Feed Sulfur vs Reformate Yield at Reactor Temperature 910 F

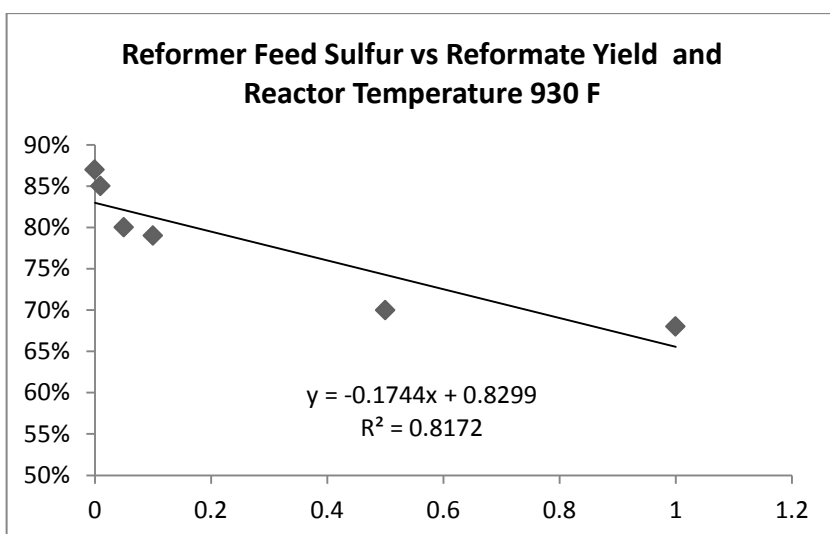


Figure 15: Reformer Feed Sulfur vs Reformate Yield and Reactor Temperature 930 F

The emissions generated by the reforming unit are from the main furnace and the inter-heaters in the reaction section. The reforming reactions are endothermic and thereby require large heat input to sustain the conversion from straight chain paraffin hydrocarbons to aromatics. Therefore, the emission coefficients are shown to increase

with reactor temperatures. The emission coefficient for the reformer is shown the following graphs:

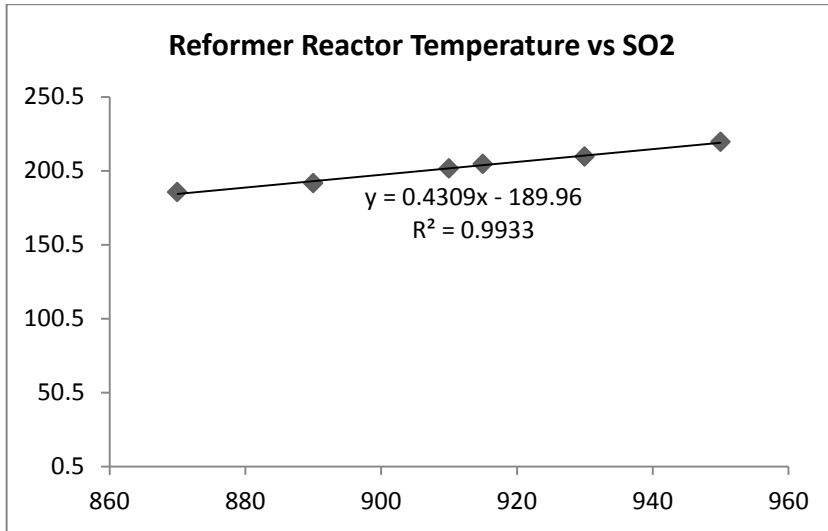


Figure 16: Reformer Reactor Temperature vs SO2

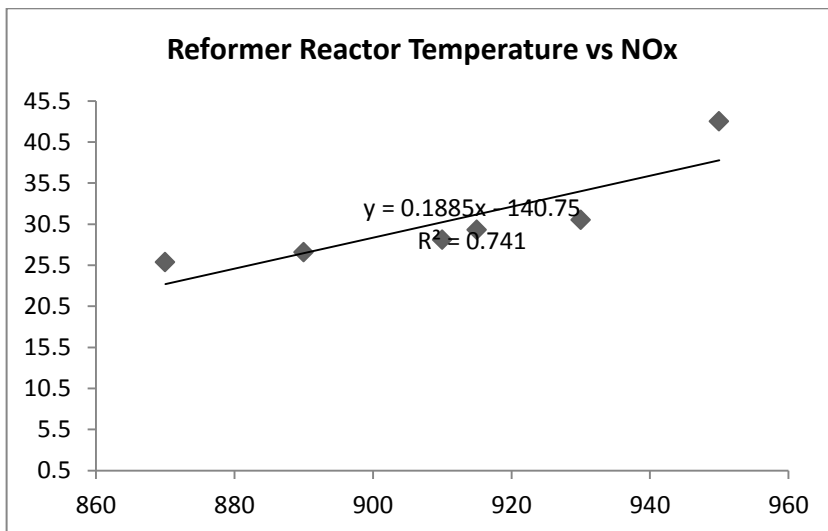


Figure 17: Reformer Reactor Temperature vs NOx

Emission coefficient as a function of feed rate also show to increase emission production with increasing process rate. With increasing rates, the duty provided by the process

heaters increase and thereby we observe an increase in the generation of SO₂ and NO_x.

This is shown in the following graph:

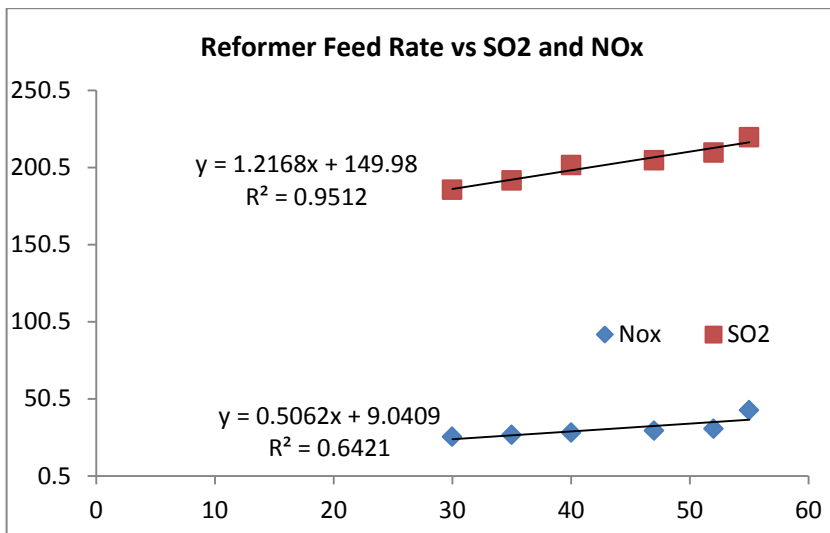


Figure 18: Reformer Feed Rate vs SO₂ and NO_x

4.1.5 Hydrocracking Unit

Hydrocrackers play a vital role in modern refining complexes where it is used to convert low value high boiling point materials to higher value material. Hydrocracking reactions are normally carried out at average catalyst temperatures between 550°F and 750°F and at reactor pressures between 1200 psig and 2000 psig (Froment et al, 1999). Large quantities of circulating hydrogen used with the feedstock prevents excessive catalyst fouling and permits long runs without catalyst regeneration (Froment et al, 1999). The temperature and pressure vary with the age of the catalyst, the product desired, and the properties of the feedstock.

Feedstock to hydrocracking unit must be prepared in order to remove catalyst poisons and to give long catalyst life. Frequently, the feedstock is hydrotreated to remove sulfur and nitrogen compounds as well as metals before it is sent to the reactor train can (Froment et

al, 1999). The feedstock is hydrotreated to saturate the olefins which can be a precursor to coking and poisoning of catalyst.

The feed to hydrocracking unit is mixed with makeup hydrogen and recycle hydrogen gas and passed through a heater to the first reactor. If the feed has not been hydrotreated, then there is a guard reactor before the first hydrocracking reactor (Froment et al, 1999). The guard reactor usually has a modified hydrotreating catalyst which is used to convert organic sulfur and nitrogen compounds to hydrogen sulfide, ammonia, and hydrocarbons to protect the precious metals catalyst in the following reactors. The hydrocracking reactor is operated at a sufficiently high temperature to convert approximately 50 vol% of the reactor effluent to material boiling below 400°F (Froment et al, 1999). In some hydrocrackers, a second stage reaction system can be used to bring the total conversion of the unconverted oil from the first-stage and second-stage recycle to 70 vol% (Froment et al, 1999).

Gasoline product yields as function of reactor temperature in the hydrocracking unit is described in Figure 19. As expected, we see increase conversion of the heavy material in the feedstock to lighter material as the reactor temperature is raised. In the simulated cases to develop the yield coefficients, similar to the other cases, yields are independent of feed quality.

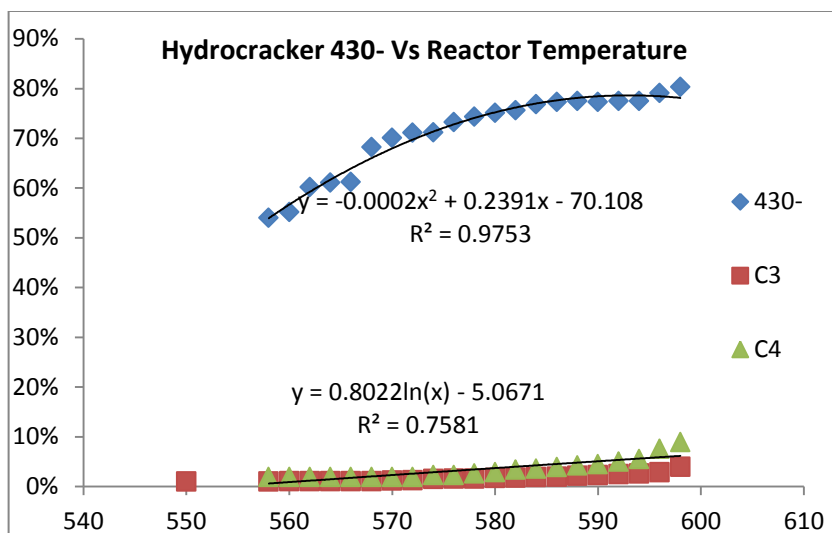


Figure 19: Hydrocracker 430- Vs Reactor Temperature

The impact of feed contaminants on the conversion process is shown in Figure 20. We observe that organic nitrogen and organic sulfur compounds have a relatively higher depressing impact on the conversion process versus the organic metal compounds. It is interesting to note the yield coefficient for the organic sulfur and nitrogen compounds is best fit with a polynomial equation versus a linear equation.

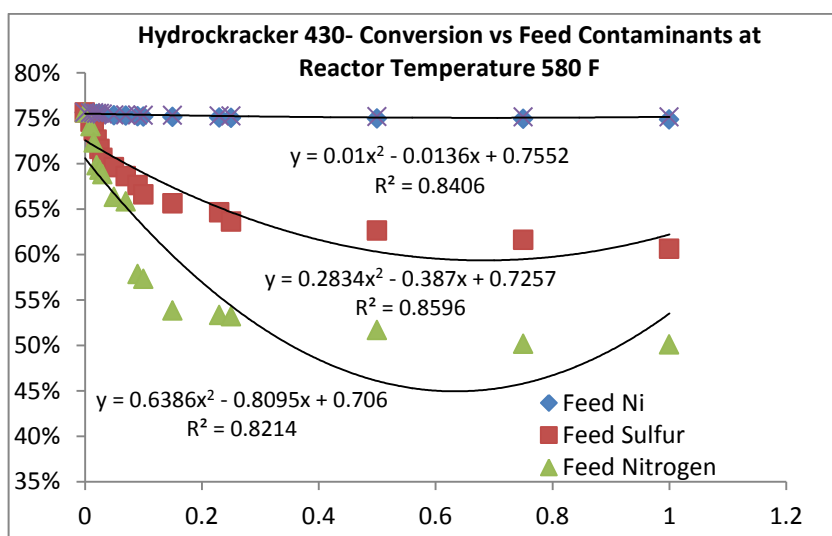


Figure 20: Hydrocracker 430- Conversion vs Feed Contaminants at Reactor Temperature 580 F

The emission coefficient for the Hydrocracking unit as a function of reactor temperature is shown in Figure 21. We observe an increasing linear relationship between SO₂ production and reactor temperatures. This is primarily due to increased duty provided by the reactor furnaces to achieve the higher reactor temperatures. Increase firing in the process heaters leads to increase consumption of refinery fuel gas, which contain small amount of sulfur via H₂S.

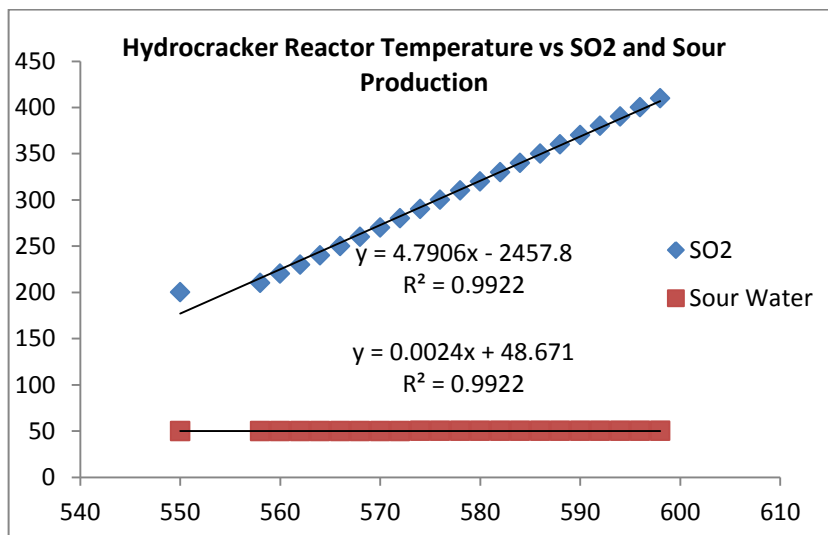


Figure 21: Hydrocracker Reactor Temperature vs SO₂ and Sour Production

The emission coefficient for the hydrocracking unit as function of process rate is given in in Figure 22, a linear relationship is observed between process rate and emission production. The SO₂ production increases due to higher firing in the process heaters with increasing process rate in order to achieve the target reactor temperature. Similar to the previous case, increasing firing in the heaters increases the SO₂ production via the H₂S present in small amounts in the fuel gas.

The sour water production at the hydrocracking unit is shown to increase with increasing process rate as shown in Figure 22. As process rate increases, the amount of wash water

required to wash the salts in the high pressure area of the reactor outlet increases therefore increasing the amount of sour water produced in the overall system.

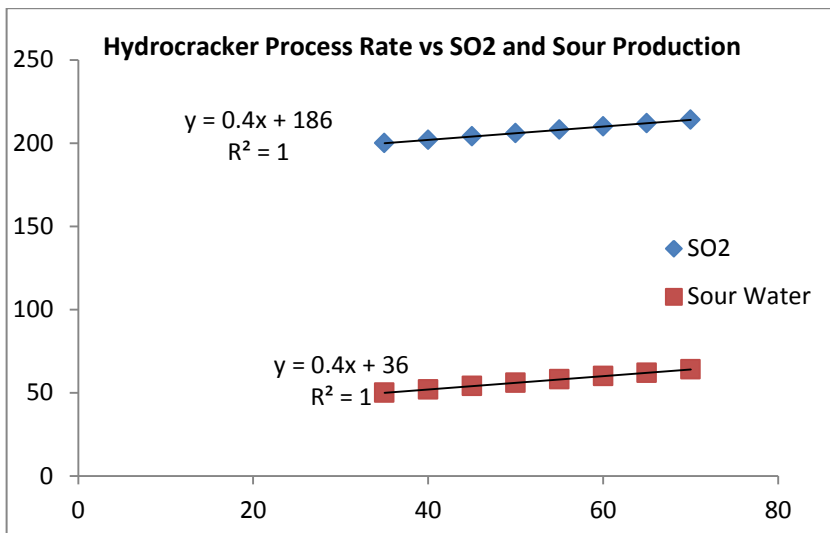


Figure 22: Hydrocracker Process Rate vs SO2 and Sour Production

4.1.6 Treating Units in Refining

Treatment units in petroleum refining industry are used to removed contaminants from intermediate processes and recover contaminants from effluent streams. Catalytic hydrotreating is an important treating process. It is used to remove about 90% of nitrogen, sulfur, oxygen, and metals from liquid petroleum fractions (Jones & Pujadó, 2006). The importance of these units is increasing as the types of crudes processed in refineries become more challenging with contaminant and non-hydrocarbon loading perspectives (Parkash, 2003).

These contaminants, if not removed, can have detrimental impact on process catalysts, the yield and quality of final products and emission from the refinery. Historically, hydrotreating was used to only protect important refinery catalysts such as reforming (Gary et al. 2001). Today, hydrotreating is being used to meet environmental guidelines

for finished product sulfur and nitrogen content as well as newer SO₂ emissions regulations (Jones & Pujadó, 2006). The type of catalyst in this process has been expressly designed to meet the desired reduction in the contaminant load.

Hydrodesulfurization is hydrotreating of sulfur removal. In a typical catalytic hydrodesulfurization unit, the feedstock is prepared by removing all oxygenates by deaerating and mixed with hydrogen preheated in a fired heater and then charged under pressure through a fixed-bed catalytic reactor (Occelli & Chianelli, 1996). In the reactor, the sulfur and nitrogen compounds in the feedstock are converted into hydrogen sulfide and ammonia.

The reaction products leave the reactor. After cooling to a low temperature, the product enters a liquid/gas separator (Occelli & Chianelli, 1996). The hydrogen-rich gas from the high-pressure separation is recycled to combine with the feedstock and the low-pressure gas stream - rich in H₂S - is sent to a gas treating unit where H₂S is removed (Occelli & Chianelli, 1996). The clean gas is then suitable as fuel for the refinery furnaces. The liquid stream is the product from hydrotreating and is normally sent to a stripping column for removal of H₂S and other undesirable components (Occelli & Chianelli, 1996). In cases where steam is used for stripping, the product is sent to a vacuum drier for removal of water. Hydrodesulfurized products are blended or used as catalytic reforming feedstock (Occelli & Chianelli, 1996).

The yield coefficient for hydrotreating units is a function of reactor temperatures for the purposes of this study. The impact of process rate on the overall yield was explored. Results of the parametric study showed that space velocity through the reactors, as

measured by overall process rate based on the range, is modeled. It has shown little impact on the overall yield of product.

The yield coefficients of the hydrotreating units (naptha and distillate) are slightly different. They both show a linear reduction in yield of the final product as temperature is raised. The loss is due to cracking of the hydrocarbon chains and production of smaller hydrocarbons which are lost in to the clean gas section. The coefficient and the representative trends modeled in HYSIS are shown in Figure 23.

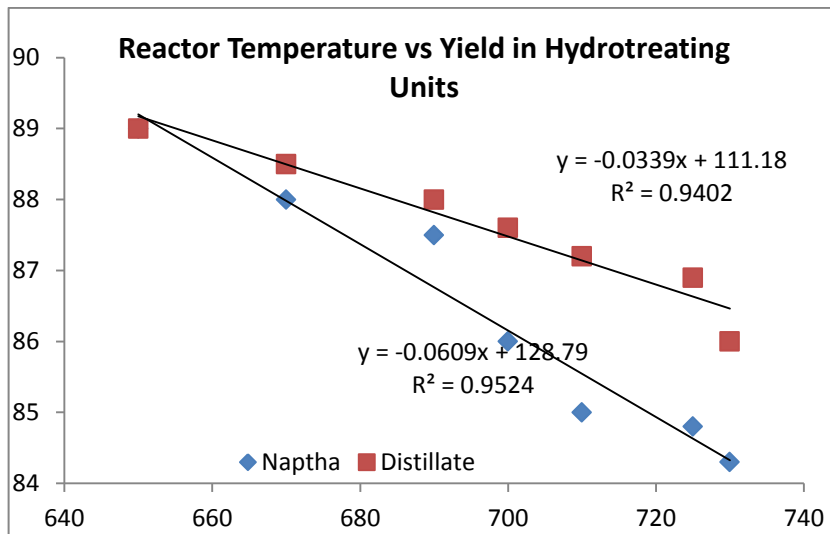


Figure 23: Reactor Temperature vs Yield in Hydrotreating Units

Air emission from hydrotreating units is generated by the process heaters, which are used to achieve the overall reactor temperatures. Similar to the other process heaters, the generation of emission from these process heaters is a function of the amount of sulphur contained in the fuel and the amount of fuel fired. Holding the amount of sulphur in the fuel constant, the amount emissions generated can be modeled as a function of process rate and reactor temperature. These functions are shown in Figure 24 and Figure 25.

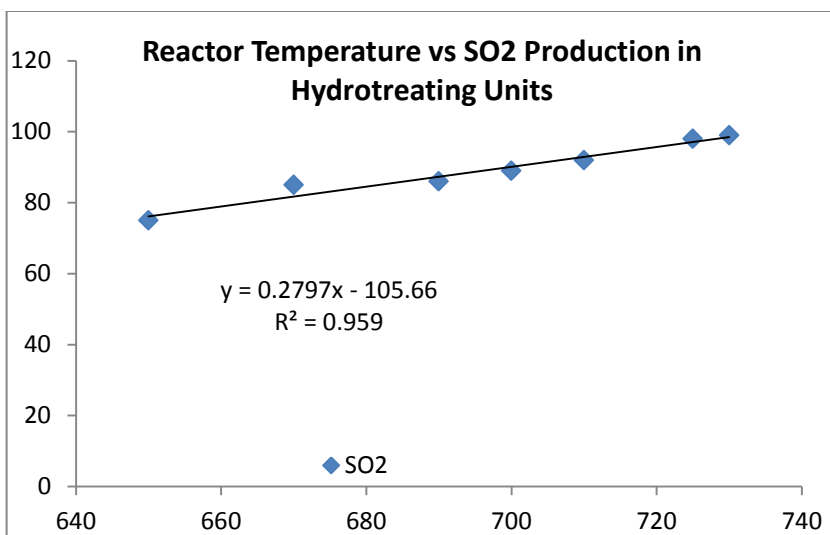


Figure 24: Reactor Temperature vs SO₂ Production in Hydrotreating Units

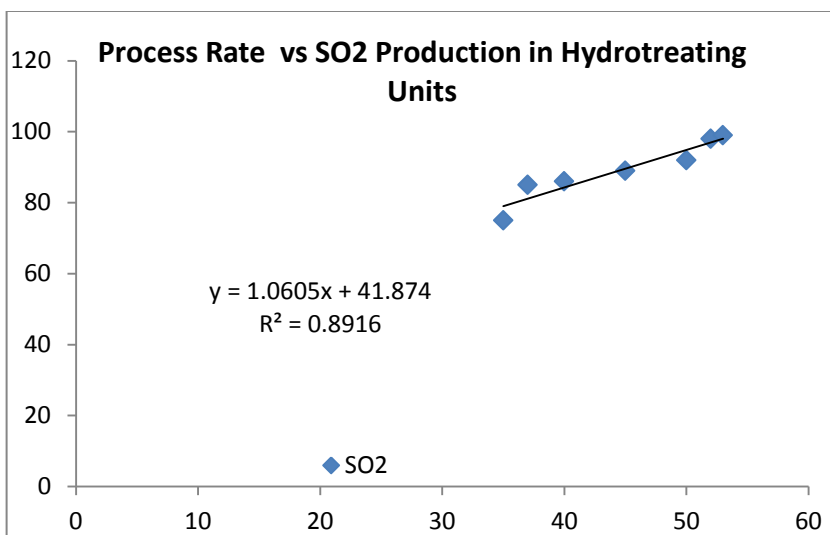


Figure 25: Process Rate vs SO₂ Production in Hydrotreating Units

5.0 Mathematical Optimization Model

The refinery model in this thesis is based the work of Elkamel and Al-Qahtani (2007), which built on a State Equipment Network (SEN) representation. The general characterization of this representation includes three elements: state, task and equipment. A state includes all streams in a process and is characterized by either quantitative or qualitative attributes or both. The quantitative characteristics include flow-rate, temperature and pressure. The qualitative characteristics include other attributes such as the phase(s) of the streams (Elkamel et al, 2007). The material streams, states and their balances are divided in to five categories: raw material, intermediates, products and fuels, utilities, and catalysts. All material balances are carried out on a mass basis, but volumetric flow rates are used in the case where quality attributes for some streams only blend on a volume basis.

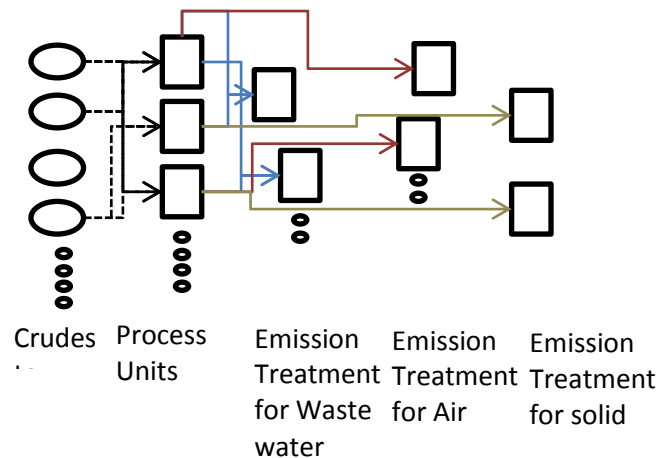


Figure 26: SEN Representation of the model

This paper differs from the Elkamel and Al-Qahtani model in two respects. First, this paper expands on the work by Elkamel and Al-Qahtani to include other process effluents streams. In their work, Elkamel and Al-Qahtani developed a model which concisely and effectively predicted air emissions in a petroleum refinery and optimized the cost effectiveness of the refinery (production cost and material costs) in an air emission constrained environment. We expand on their work to include wastewater generation and solid waste generation in refining. Also, this paper reduces the complexity of the refinery model by removing inter-trading of crude oil. This paper has an ultimate goal of applying this model in a North American refinery, where crude trading is conducted outside of the refinery's influence.

5.1 Refinery Model

The problem is formulated as a mixed integer linear program (MILP). Binary variables are used for selecting the optimal pollutant control strategies . In the initial formulation, the model is not linear and therefore must be linearized. Linearity in the model was achieved by defining components flows instead of individual flows. Associated fractions and exact linearization techniques will be explained in the following paragraphs (Elkamel et al, 2007).

To show the refinery material balance, constraint 1 shown, as equation 1, depicts the refinery material throughput $z_{cr,p,i}$ to the pipestill (sometimes known as the CDU) units $p \in P$ at plant $i \in I$ from each crude type $cr \in CR$ is equal to the available $S_{cr,i}$. $S_{cr,i}$ represents the total crude supply to each pipestill.

$$z_{cr,p,i} = S_{cr,i} \quad \forall cr \in CI, i \in I \quad \text{Equation 1}$$

Where $p \in P$ {Set of CDU process \forall plant i }

Downstream from the pipestill, the intermediate conversion units are ready to receive the distilled crude. The intermediate stream in the refinery is complex. Some streams are recycle or a product from one intermediate process unit and act as the feed to other intermediate process units. Therefore, the flow for each stream can assume both a positive and a negative value depending on the source and destination. Constraint 2, via Equation 2, attempts to capture the duality of flow for the intermediate streams. We capture the flow via the coefficient $a_{cr,ci,p}$ which can assume either a positive or a negative sign depending on if it is an input or an output from a specific unit. This constraint is essentially a material balance for the intermediate streams. It ensures that all intermediate streams are either consumed in the final product $w_{cr,ci,cfr,i}$ or in the refinery fuel system $w_{cr,ci,rf,i}$

$$\begin{aligned} \sum_{p \in P} a_{cr,ci,i,p} z_{cr,p,i} - \sum_{cfr \in CFR} w_{cr,ci,cfr,i} \\ - \sum_{rf \in Fuel} w_{cr,ci,rf,i} = 0 \\ \forall cr \in CR \quad ci \in CI \quad i \in I \end{aligned} \quad \text{Equation 2}$$

Constraint 3, shown as Equation 3, conducts the material balance on each product stream in each refinery. Mathematically, we can express product from the refinery as the difference between all the intermediate streams generated and the intermediate streams that have been subsumed in to the fuel system. This expression maintains the general

flow path of the refinery and maintains material balance. In Equation 3, $xf_{cfr,i}$ represent the product streams from each refinery, $w_{cr,ci,cfr,i}$ represent intermediate streams used in the final product, and $w_{cr,ci,rf,i}$ represent intermediate streams that are subsumed and used in the fuel system.

$$\sum_{cr \in CR} \sum_{ci \in CB} w_{cr,ci,cfr,i} - \sum_{cr \in CR} \sum_{rf \in Fuel} w_{cr,cfr,rf,i} = xf_{cfr,i} \quad \forall cfr \in CFR \quad i \in I$$

Equation 3

Many of the qualities that are critical for producing saleable products blend on a volumetric basis and thus far we have been conducting material balancing on a mass basis. In Constraint 4, shown as Equation 4, we convert from mass flow rate $xf_{cfr,i}$ to volumetric flow rate $xvf_{cfr,i}$ by utilizing specific gravities $sg_{ci,cr}$ for each crude $cr \in CR$ and intermediate stream $ci \in CB$

$$\sum_{cr \in CR} \sum_{ci \in CB} \frac{w_{cr,ci,cfr,i}}{sg_{ci,cr}} = xvf_{cfr,i} \quad \forall cfr \in CFR, i \in I$$

Equation 4

In Constraint 5, shown as Equation 5, we conduct a fuel system balance. This model does not allow for selling of excess fuel generated in the refineries. The balance shown in Equation 5 states all generated fuel from both intermediate streams and final products

must be consumed by the process heaters and boilers. As such, the heat content of the fuels system represented by $cv_{re,ci,I}$ is the caloric/btu value of the fuels. $w_{cr,ci,rf,i}$ represents intermediate streams used in the fuels and $w_{cr,ci,rf,i}$ represent final products used in the fuel system. The consumption of the fuel by the process heaters and boils is represented by matrix $\beta_{cr,rf,i,p}$.

$$\begin{aligned} & \sum_{ci \in \text{Fuel}} cv_{rf,ci,i} w_{cr,ci,rf,i} \\ & + \sum_{cfr \in \text{Fuel}} w_{cr,cfr,rf,i} \\ & - \sum_{p \in P} \beta_{cr,rf,i,p} z_{cr,p,i} = 0 \quad \forall cr \in Cr, \quad rf \in \text{Fuel}, I \in I \end{aligned}$$

Equation 5

In constraint 6, shown as Equation 6, we attempt to stipulate product quality limitation as either an upper limit, lower limit, or both. Each product streams, represented by a final product $w_{cr,ci,cfr,i}$, has market or legislative limitation. One example is motor gasoline or MOGAS, which has a minimum octane, maximum RVP. For stream qualities that blend on a mass basis $q \in Q_w$ the flowing will hold:

$$\begin{aligned} & \sum_{cr \in CR} \sum_{ci \in CB} \left[att_{cr,ci,q \in Q_v} \frac{w_{cr,ci,cfr,i}}{sg_{ci,cr}} + att_{cr,ci,q \in Q_w} \left[w_{cr,ci,cfr,i} - \sum_{rf \in \text{Fuel}} w_{cr,cfr,rf,i} \right] \right] \\ & \geq q_{cr,ci,q \in Q_v}^L x_{vf_{cfr,i}} + q_{cr,ci,q \in Q_w}^L x_{f_{cfr,i}} \quad \forall cfr \in CFR, q \\ & = [Q_w, Q_v], i \in I \end{aligned}$$

Equation 6

Similarly, Constraint 7, shown as Equation 7, is a quality limit set for stream qualities that blend on volume basis $q \in Q_v$

$$\begin{aligned} \sum_{cr \in CR} \sum_{ci \in CB} & \left[att_{cr,ci,q \in Q_v} \frac{w_{cr,ci,cfr,i}}{sg_{ci,cr}} + att_{cr,ci,q \in Q_w} \left[w_{cr,ci,cfr,i} - \sum_{rf \in Fuel} w_{cr,cfr,rf,i} \right] \right] \\ & \geq q_{cr,ci,q \in Q_v}^U xvf_{cfr,i} + q_{cr,ci,q \in Q_w}^U xf_{cfr,i} \quad \forall cfr \in CFR, q \\ & = [Q_w, Q_v], i \in I \end{aligned}$$

Equation 7

Constraint 8, shown as Constraint 8, ensures each process unit is operating within design rates and severities. Process units which have mode based operation, $\gamma_{m,p}$ represents a binary matrix for the assignment of production to process operating mode.

$$\min C_{m,i} \leq \sum_{p \in P} \gamma_{m,p} \sum_{cr \in CR} z_{cr,p,i} \leq \max C_{m,i} \quad \forall m \in M, \quad i \in I$$

Equation 8

Constraint 9, shown as Equation 9, ensures that the demand for each product is met by the refinery production units.

$$\sum_{i \in I} [xf_{cfr,i}] \geq d_{cfr} \quad \forall cfr$$

Equation 9

The objective function in the overall refinery model minimizes the annualized cost associated with raw material costs and operating costs. The objective function considered for the refinery wide model is as follows:

Minimize

$$\text{MIN} \sum_{cr \in CR} \sum_{i \in I} \text{CRcost}_{cr} S_{cr,i} + \sum_{p \in P} \text{EOcost}_p \sum_{cr \in CR} \sum_{i \in I} z_{cr,p,i}$$

Equation 10

5.2 Solid Waste Optimization Model

The solid waste sub model attempts to establish the total waste effluent generated by each process units as crude and intermediate streams are processed. Solid waste generated by the refinery process streams can be described with Equation 11:

$$R_{v,l} = \sum_{fs} DW_{fs} \sum_v PR_v \quad \forall v \in V$$

Equation 11

Where DW_{fs} represents the solid waste generation factor and PR_v represents process unit rate.

In Equation 12, a refinery wide solid waste balance is conducted:

$$R_{v,l} = \sum_0 R_{v,l,o} Y_{v,l,o} \quad \forall \quad v \in V, o \in O$$

Equation 12

Where $v \in V$ represent effluents of a specific pollutant $l \in L$ over multiple mitigation $o \in O$

This derivation of waste generation gives rise to a non-linear mixed integer term. In order to linearize, branch and bound approach was chosen. This allows for the generation of converging sequences of valid upper and lower bounds (Glover et al, 1975). With this approach, if the problem is not infeasible or the bounds are not excessively restrictive, then an upper bound is generated through the solution of the original non-convex MINLP restricted to the current domain. Although this adds more repetitive search to the model, this route is attractive because the NLP sub-problem is relatively inexpensive to solve.

As such, we redefine the binary variable $Y_{v,l,o}$ in terms of the following set the binary variable: $Y_{v,l,feedswitch}$ and $Y_{v,l,capture}$ using upper and lower bounds on the waste generated. $Y_{v,l,feedswitch}$ representing switching feed at the process unit in order to achieve the target emission, and $Y_{v,l,capture}$ representing the route of applying one of the specified capture technologies in order to meet the emission target. The above equation can be re-written as a set of inequality constraints shown as follows:

$$R_{v,l} \leq DW_{fs} PR_v + R_{v,l}^+ \sum_{o \in \text{feedswitch}} Y_{v,l,\text{feedswitch}} + R_{v,l}^+ \sum_{o \in \text{capture}} Y_{v,l,\text{capture}} \quad \forall v \in V, l \in L$$

Equation 13

$$R_{v,l} \geq DW_{fs} PR_v - R_{v,l}^+ \sum_{o \in \text{feedswitch}} Y_{v,l,\text{feedswitch}} - R_{v,l}^+ \sum_{o \in \text{capture}} Y_{v,l,\text{capture}} \quad \forall v \in V, l \in L$$

Equation 14

$R_{v,l}^+$ represents the upper limit on each waste l from each production unit v .

The model is given the flexibility for feed switching in order to evaluate the impact on waste generation. Equation 15 and Equation 16 depict the set of inequalities for the upper and lower limit for waste generation for a given set of feeds. The set of feed switches are defined as fs to fs^s .

$$R_{v,l} \leq DW_{fs^s} PR_v + R_{v,l}^+ \left(1 - \sum_{o \in \text{feedswitch}} Y_{v,l,\text{feedswitch}} \right) + R_{v,l}^+ \sum_{o \in \text{feedswitch}} Y_{v,l,\text{capture}} \quad \forall v \in V, l \in L$$

Equation 15

$$R_{v,l} \geq DW_{fs^s} PR_v - R_{v,l}^+ \left(1 - \sum_{o \in \text{feedswitch}} Y_{v,l,\text{feedswitch}} \right) - R_{v,l}^+ \sum_{o \in \text{feedswitch}} Y_{v,l,\text{capture}} \quad \forall v \in V, l \in L$$

Equation 16

Similarly, applying the above logic to the capture approach yields the following:

$$R_{v,l} \leq DW_{fs} PR_v (1 - \pi_{\text{capture}}) + R_{v,l}^+ \sum_{o \in \text{feedswitch}} Y_{v,l,\text{feedswitch}} \\ + R_{v,l}^+ \left(1 - \sum_{o \in \text{feedswitch}} Y_{v,l,\text{capture}} \right) \quad \forall v \in V, l \in L$$

Equation 17

$$R_{v,l} \geq DW_{fs} PR_v (1 - \pi_{\text{capture}}) - R_{v,l}^+ \sum_{o \in \text{feedswitch}} Y_{v,l,\text{feedswitch}} \\ - R_{v,l}^+ \left(1 - \sum_{o \in \text{feedswitch}} Y_{v,l,\text{capture}} \right) \quad \forall v \in V, l \in L$$

Equation 18

π_{capture} represents the efficiency and effectiveness of a specific waste capture technology to reduce the overall waste generated, leaving the process as effluent for a given production or process unit.

This project will stipulate that only one capture and mitigation alternatives will be applied for each solid waste type.

$$\sum_{o \in \text{feedswitch}} Y_{v,l,\text{feedswitch}} \leq 1 \quad \forall v \in V, l \in L$$

Equation 19

$$\sum_{o \in \text{feedswitch}} Y_{v,l,\text{capture}} \leq 1 \quad \forall v \in V, l \in L$$

Equation 20

$$\sum_{o \in \text{feedswitch}} Y_{v,l,\text{capture}} + \sum_{o \in \text{feedswitch}} Y_{v,l,\text{feedswitch}} \leq 1 \quad \forall v \in V, l \in L$$

Equation 21

Feed switch will incur added inflexibilities to the model which will be captured as a cost. The cost of switching feed qualities to process units in order to affect solid waste generation will be described by the variable $\sigma_{v,l}$. The annualized cost of operating a capture process for the purpose of limiting solid waste generation will be described by the variable $\mu_{v,l}$. The following constraints can be added to the submodel:

$$HG_{v,l}^- \sum_{o \in \text{feedswitch}} Y_{v,l,\text{feedswitch}} \leq \sigma_{v,l} \leq HG_{v,l}^+ \sum_{o \in \text{feedswitch}} Y_{v,l,\text{feedswitch}} \quad \forall v \in V, l \in L$$

Equation 22

$$\begin{aligned} \text{COST}_{\text{feedswitch}} - HG_{v,l}^+ \left[1 - \sum_{o \in \text{feedswitch}} Y_{v,l,\text{feedswitch}} \right] &\leq \sigma_{v,l} \\ &\leq \text{COST}_{\text{feedswitch}} - HG_{v,l}^- \left[1 - \sum_{o \in \text{feedswitch}} Y_{v,l,\text{feedswitch}} \right] \quad \forall v \in V, l \in L \end{aligned}$$

Equation 23

$HG_{v,l}^-$ and $HG_{v,l}^+$ represent the upper and lower limit on the cost of switching feed qualities to the process units. These limit and are given values to provide proper upper and lower limits. Similarly, a set of inequalities can be defined for cost of process capture $\mu_{v,l}$.

$$HE_{v,l}^- \sum_{o \in \text{capture}} Y_{v,l,\text{capture}} \leq \mu_{v,l} \leq HE_{v,l}^+ \sum_{o \in \text{capture}} Y_{v,l,\text{capture}} \quad \forall v \in V, l \in L$$

Equation 24

$$\begin{aligned} \text{COST}_{\text{capture}} - HE_{v,l}^+ \left[1 - \sum_{o \in \text{capture}} Y_{v,l,\text{feedswitch}} \right] &\leq \mu_{v,l} \\ &\leq \text{COST}_{\text{capture}} - HE_{v,l}^- \left[1 - \sum_{o \in \text{capture}} Y_{v,l,\text{capture}} \right] \quad \forall v \in V, l \in L \end{aligned}$$

Equation 25

As above, $HE_{v,l}^-$ and $HE_{v,l}^+$ represent the upper and lower limit on the cost of operating capture technology for each given effluent. These limits and are given values to provide proper upper and lower limits.

The objective function, which minimizes raw material costs and operating costs, can be written as follows:

$$\text{MIN} \sum_{cr \in CR} \sum_{i \in I} \text{CRcost}_{cr} S_{cr,i} + \sum_{p \in P} \text{EOcost}_p \sum_{cr \in CR} \sum_{i \in I} z_{cr,p,i} + \sum_v \sum_l \mu_{v,l} + \sum_v \sum_l \sigma_{v,l}$$

Equation 26

5.3 Wastewater Optimization Model

The wastewater sub model is designed to minimize the costs associated with producing and treating waste water that is generated as part of process unit operation while meeting product demands. Wastewater generated in the refinery is calculated through Equation 27:

$$A_{x,n} = \sum_{fs} AW_{fs} \sum_v PR_x \quad \forall x \in X$$

Equation 27

Where AW_{fs} represents the wastewater generation factor and PR_x represents process unit rate.

In Equation 28, a refinery wide wastewater balance is conducted:

$$A_{x,n} = \sum_g A_{x,n} Y_{x,n,g} \quad \forall x \in X, n \in N$$

Equation 28

Where $x \in X$ represent effluents of a specific pollutant $n \in N$ over multiple mitigation $g \in G$ and $Y_{x,n,g}$ represents a binary selection variable.

Similar to the sub-model presented for solid waste, the water sub-model gives rise to non-linearity that we propose to linearize by using the branch and bound method. As such, $Y_{x,n,g}$ can be redefined in terms of $Y_{x,n,redconsump}$ and $Y_{x,n,treat}$ using upper bounds on the waste generated.

Equation 28 can be re-defined as a set of inequality constraints shown as follows:

$$A_{x,n} \leq AW_{fs} PR_v + A_{x,n}^+ \sum_{o \in redconsump} Y_{x,n,redconsump} + A_{x,n}^+ \sum_{o \in treat} Y_{x,n,treat} \quad \forall x \in X, n \in N$$

Equation 29

$$A_{x,n} \geq AW_{fs}PR_v - A_{x,n}^+ \sum_{o \in \text{redconsump}} Y_{x,n,\text{redconsump}} - A_{x,n}^+ \sum_{o \in \text{treat}} Y_{x,n,\text{treat}} \quad \forall x \in X, n \in N$$

Equation 30

$A_{x,n}^+$ represents the upper limit on each waste n from each production unit x .

Reducing the water consumption by altering unit operation from the base can be given as follows:

$$A_{x,n} \leq AW_{fs}PR_v + A_{x,n}^+ \left(1 - \sum_{o \in \text{redconsump}} Y_{x,n,\text{redconsump}} \right) + A_{x,n}^+ \sum_{o \in \text{treat}} Y_{x,n,\text{treat}} \quad \forall x \in X, n \in N$$

Equation 31

$$A_{x,n} \geq AW_{fs}PR_v - A_{x,n}^+ \left(1 - \sum_{o \in \text{redconsump}} Y_{x,n,\text{redconsump}} \right) - A_{x,n}^+ \sum_{o \in \text{treat}} Y_{x,n,\text{treat}} \quad \forall x \in X, n \in N$$

Equation 32

The impact and diversion of waste by applying capture technology to the discharge of wastewater from the refinery can be represented as follows:

$$A_{x,n} \leq AW_{fs} PR_v (1 - \tau_{treat}) + A_{x,n}^+ \sum_{o \in redconsump} Y_{x,n,redconsump} \\ + A_{x,n}^+ \left(1 - \sum_{o \in treat} Y_{x,n,treat} \right) \quad \forall x \in X, n \in N$$

Equation 33

$$A_{x,n} \geq AW_{fs} PR_v (1 - \tau_{treat}) - A_{x,n}^+ \sum_{o \in redconsump} Y_{x,n,redconsump} \\ - A_{x,n}^+ \left(1 - \sum_{o \in treat} Y_{x,n,treat} \right) \quad \forall x \in X, n \in N$$

Equation 34

τ_{treat} represents the efficiency, ranging from 0 to 1, of a specific wastewater treatment technology or approach. The efficiency term represents the extent to which the overall waste generated and leaving the process as effluent is reduced for a given production or process unit.

Similar to solid waste case, only one capture alternative will be applied for each wastewater type.

$$\sum_{o \in redconsump} Y_{x,n,redconsump} \leq 1 \quad \forall x \in X, n \in N$$

Equation 35

$$\sum_{o \in treat} Y_{x,n,treat} \leq 1 \quad \forall x \in X, n \in N$$

Equation 36

$$\sum_{o \in \text{redconsump}} Y_{x,n,\text{redconsump}} + \sum_{o \in \text{treat}} Y_{x,n,\text{treat}} \leq 1 \quad \forall x \in X, n \in N$$

Equation 37

The cost to reduce process water consumption at the expense of potential product quality downgrades in the process units in order to affect waste water generation will be described by the variable $\vartheta_{x,n}$. The annualized cost of operating a wastewater process for the purpose of limiting wastewater generation will be described by the variable $\rho_{x,n}$. The following constraints can be added to the sub-model:

$$AG_{x,n}^- \sum_{o \in \text{redconsump}} Y_{x,n,\text{redconsump}} \leq \vartheta_{x,n} \leq AG_{x,n}^+ \sum_{o \in \text{redconsump}} Y_{x,n,\text{redconsump}} \quad \forall x \in X, n \in N$$

Equation 38

$$\begin{aligned} \text{COST}_{\text{redconsump}} - AG_{x,n}^+ \left[1 - \sum_{o \in \text{redconsump}} Y_{x,n,\text{redconsump}} \right] &\leq \vartheta_{x,n} \\ &\leq \text{COST}_{\text{redconsump}} - AG_{x,n}^- \left[1 - \sum_{o \in \text{redconsump}} Y_{x,n,\text{redconsump}} \right] \quad \forall x \in X, n \in N \end{aligned}$$

Equation 39

$AG_{v,l}^-$ and $AG_{v,l}^+$ represent the upper and lower limit on the cost of switching feed qualities to the process units. Similarly, we can define a set of inequalities for the cost of process capture $\mu_{v,l}$.

$$AE_{x,n}^- \sum_{o \in \text{treat}} Y_{x,n,\text{treat}} \leq \rho_{x,n} \leq AE_{x,n}^+ \sum_{o \in \text{treat}} Y_{x,n,\text{treat}} \quad \forall x \in X, n \in N$$

Equation 40

$$\begin{aligned} \text{COST}_{\text{treat}} - AE_{x,n}^+ \left[1 - \sum_{o \in \text{treat}} Y_{x,n,\text{treat}} \right] &\leq \rho_{x,n} \\ &\leq \text{COST}_{\text{treat}} - AE_{x,n}^- \left[1 - \sum_{o \in \text{treat}} Y_{x,n,\text{treat}} \right] \quad \forall x \in X, n \in N \end{aligned}$$

Equation 41

As above, $AG_{x,n}^-$ and $AG_{x,n}^+$ represent the upper and lower limit on the cost of operating treatment technology for each given effluent.

The objective function can be written as follows:

$$\text{MIN} \sum_{cr \in CR} \sum_{i \in I} \text{CRcost}_{cr} S_{cr,i} + \sum_{p \in P} \text{EOcost}_p \sum_{cr \in CR} \sum_{i \in I} z_{cr,p,i} + \sum_x \sum_n \vartheta_{x,n} + \sum_x \sum_n \rho_{x,n}$$

Equation 42

5.4 Air Emission Optimization Model

The air emission sub-model is designed to minimize the costs associated with producing and treating air emissions that are generated as part of process unit operation while meeting product demands. Air emissions generated in the refinery is depicted by Equation 43:

$$E_{m,k} = \sum_{rf} Ef_{rf} \sum_m FC_m \quad \forall m \in M$$

Equation 43

Where Ef_{rf} represents the wastewater generation factor and FC_m represents process unit rate.

Refinery wide effluent air emissions are calculated by Equation 44.

$$E_{m,k} = \sum_j E_{m,k} Y_{m,k,j} \quad \forall m \in M, k \in K$$

Equation 44

Where $m \in M$ represent effluents of a specific pollutant $k \in K$ over multiple mitigation $j \in J$ and $Y_{m,k,j}$ represents a binary selection variable.

Similar to previous sub-models presented, the air emission sub-model gives rise to non-linearity that we propose to linearize by using the branch and bound method. As such, a binary variable $Y_{m,k,j}$ can be defined in terms of either fuel switching in the refinery

$Y_{m,k,switch}$ or capture technology $Y_{m,k,capture}$ using appropriate upper bounds on different emissions.

Equation 45 can be re-defined as a set of inequality constraints shown as follows:

$$E_{m,k} \leq Ef_{rf}FC_m + E_{m,k}^+ \sum_{j \in switch} Y_{m,k,switch} + E_{m,k}^+ \sum_{j \in capture} Y_{m,k,capture} \quad \forall m \in M, k \in K$$

Equation 45

$$E_{m,k} \geq Ef_{rf}FC_m - E_{m,k}^+ \sum_{j \in switch} Y_{m,k,switch} - E_{m,k}^+ \sum_{j \in capture} Y_{m,k,capture} \quad \forall m \in M, k \in K$$

Equation 46

Where $E_{m,k}^+$ represents the upper limit on each waste n

The impact of fuel switch on the air emission generated by the process can be given as follows:

$$E_{m,k} \leq Ef_{rf'}FC_m + E_{m,k}^+ \left[1 - \sum_{j \in switch} Y_{m,k,switch} \right] + E_{m,k}^+ \sum_{j \in capture} Y_{m,k,capture} \quad \forall m \in M, k \in K$$

Equation 47

$$E_{m,k} \geq Ef_{rf'}FC_m - E_{m,k}^+ \left[1 - \sum_{j \in \text{switch}} Y_{m,k,\text{switch}} \right] \\ - E_{m,k}^+ \sum_{j \in \text{capture}} Y_{m,k,\text{capture}} \quad \forall m \in M, k \in K$$

Equation 48

Where rf represents base fuel fired in the process heaters and optional alternative rf' is available in the refinery with differing qualities.

Applying the above logic to the capture process case yields the following inequality:

$$E_{m,k}^+ \left[1 - \sum_{j \in \text{capture}} Y_{m,k,\text{capture}} \right] \quad \forall m \in M, k \in K$$

Equation 49

$$E_{m,k} \geq Ef_{rf}FC_m(1 - \varepsilon_{\text{capture}}) - E_{m,k}^+ \sum_{j \in \text{switch}} Y_{m,k,\text{switch}} \\ - E_{m,k}^+ \left[1 - \sum_{j \in \text{capture}} Y_{m,k,\text{capture}} \right] \quad \forall m \in M, k \in K$$

Equation 50

$\varepsilon_{\text{capture}}$ represents the efficiency, ranging from 0 to 1, of a specific air emission treatment technology to reduce the overall emission leaving the process as effluent for a given production or process unit.

Similar previous sub-models, there will only be one capture alternative will be applied for each air emission type.

$$\sum_{j \in \text{switch}} Y_{m,k,\text{switch}} \leq 1 \quad \forall m \in M, k \in K$$

Equation 51

$$\sum_{j \in \text{capture}} Y_{m,k,\text{capture}} \leq 1 \quad \forall m \in M, k \in K$$

Equation 52

$$\sum_{j \in \text{switch}} Y_{m,k,\text{switch}} \leq 1 + \sum_{j \in \text{capture}} Y_{m,k,\text{capture}} \quad \forall m \in M, k \in K$$

Equation 53

$\theta_{m,k}$, represents the annualized cost of fuel switching. $\varphi_{m,k}$ represents the annualized capture process cost. The following constraints can be added to the sub-model:

$$DS_{m,k}^- \sum_{j \in \text{switch}} Y_{m,k,\text{switch}} \leq \theta_{m,k} \leq DS_{m,k}^+ \sum_{j \in \text{switch}} Y_{m,k,\text{switch}} \quad \forall m \in M, k \in K$$

Equation 54

$$\begin{aligned} Cost_{\text{switch}} E_{m,k} - DS_{m,k}^+ \left[1 - \sum_{j \in \text{switch}} Y_{m,k,\text{switch}} \right] &\leq \theta_{m,k} \\ &\leq Cost_{\text{switch}} E_{m,k} - DS_{m,k}^- \left[1 - \sum_{j \in \text{switch}} Y_{m,k,\text{switch}} \right] \quad \forall m \in M, k \in K \end{aligned}$$

Equation 55

$DS_{m,k}^+$ and $DS_{m,k}^-$ represent the upper and lower limit on the cost of the fuel switch case on the process units. Similarly, a set of inequalities can be redefined for the cost of process capture $\varphi_{m,k}$.

$$DC_{m,k}^- \sum_{j \in \text{capture}} Y_{m,k,\text{capture}} \leq \varphi_{m,k} \leq DC_{m,k}^+ \sum_{j \in \text{capture}} Y_{m,k,\text{capture}} \quad \forall m \in M, k \in K$$

Equation 56

$$\begin{aligned} Cost_{\text{capture}} E_{m,k} - DC_{m,k}^+ \left[1 - \sum_{j \in \text{capture}} Y_{m,k,\text{capture}} \right] &\leq \varphi_{m,k} \\ &\leq Cost_{\text{capture}} E_{m,k} - DC_{m,k}^- \left[1 - \sum_{j \in \text{capture}} Y_{m,k,\text{capture}} \right] \quad \forall m \in M, k \\ &\in K \end{aligned}$$

Equation 57

As above, $DC_{m,k}^-$ and $DC_{m,k}^+$ represent the upper and lower limit on the cost of operating treatment technology for each given effluent.

The objective function can be written as follows:

$$\begin{aligned} \text{MIN} \sum_{cr \in CR} \sum_{i \in I} CRcost_{cr} S_{cr,i} &+ \sum_{p \in P} EOcost_p \sum_{cr \in CR} \sum_{i \in I} z_{cr,p,i} + \sum_m \sum_k \theta_{m,k} \\ &+ \sum_m \sum_k \varphi_{m,k} \end{aligned}$$

Equation 58

6.0 Illustrative case studies

In this section, performance of the proposed model and the subsequent sub models will be illustrated on an existing North American refinery. Initially, refinery connectivity and the existing process unit will be illustrated. The objective of the model is to sustain or improve profitability of the refinery under different constraints. The decision matrix and model results will be shown. An in-depth analysis of the impacts of decisions, optimality, and their subsequent bearing on both profitable operation and emission reduction will be detailed.

6.1 Case Layout

The refinery layout will be shown as a process flow diagram. Initially a base case with no emission mitigation in place will be conducted for data gathering purposes. Once this is completed, follow-up cases will impose the sub model constraints and perform optimization studies. The modeling system GAMS was used as the optimization program.

Figure 27 depicts the process flow diagram for the refinery. The refinery has a CDU with a name plate processing capability of 225,000 barrels per day. The crude being processed contains 2.5 weight percent sulfur and 1010 parts per million organic nitrogen content on average. The CDU has three parallel preheat trains each feeding three separate process heaters. The process heaters in the CDU unit along with VDU unit fire primarily refinery fuel gas along with vacuum vent gases. The vacuum vent contains 15 ppm hydrogen sulfide (H₂S). The effluent gasses from these process heaters are not treated in the base case. The CDU and VDU separate crude oil into the fractions of different boiling points. These fractions are further refined in the upgrading units.

The light straight run Naphtha stream from the CDU is sent to a light oil merox treatment for mercaptain removal. The heavy straight run naphtha stream is sent to the reforming unit via the pre-treatment section. The refined oil stream is hydrofined to jet oil production. The heavy distillate stream is sent for hydrotreating with an ultimate destination of diesel blending. The atmospheric gas oil along with all the VDU side products are sent to the FCC unit for cracking. The VDU bottoms products are sent for heavy hydrofining with the ultimate target of heavy fuel oil blending.

The refinery contains a single UOP slide valve designed Fluid Catalytic cracking unit with a processing capacity of 65,000 barrels per day. The LPG from the FCC is sent to refinery fuel gas production. The Butylene from the FCC is sent to the alkylation unit for alkylate production. The Naphtha from the FCC is sent for hydrofining and then to gasoline blending. The cracked gas oil from the FCC is sent to hydrofining and then to diesel blending. The bottoms product from the FCC is sent to heavy fuel oil.

The refinery has two catalytic reforming units. One UOP CCR technology and the other EXXON semi regenerator design. The naphtha processed is a mix of refinery-based heavy straight run naphtha and purchased naphtha. The hydrogen is sent to the compression unit and is distributed to all the low pressure and high pressure hydroprocessing units in the refinery. The reformate products are primarily sent to gasoline blending while the Benzene and Toluene are sold as chemical base products.

Table 1 shows the effluent emissions that will be studied in this case study. Reprocessing of waste, fuel switching in fired heaters, and boilers and refinery feed switches will be explored as options.

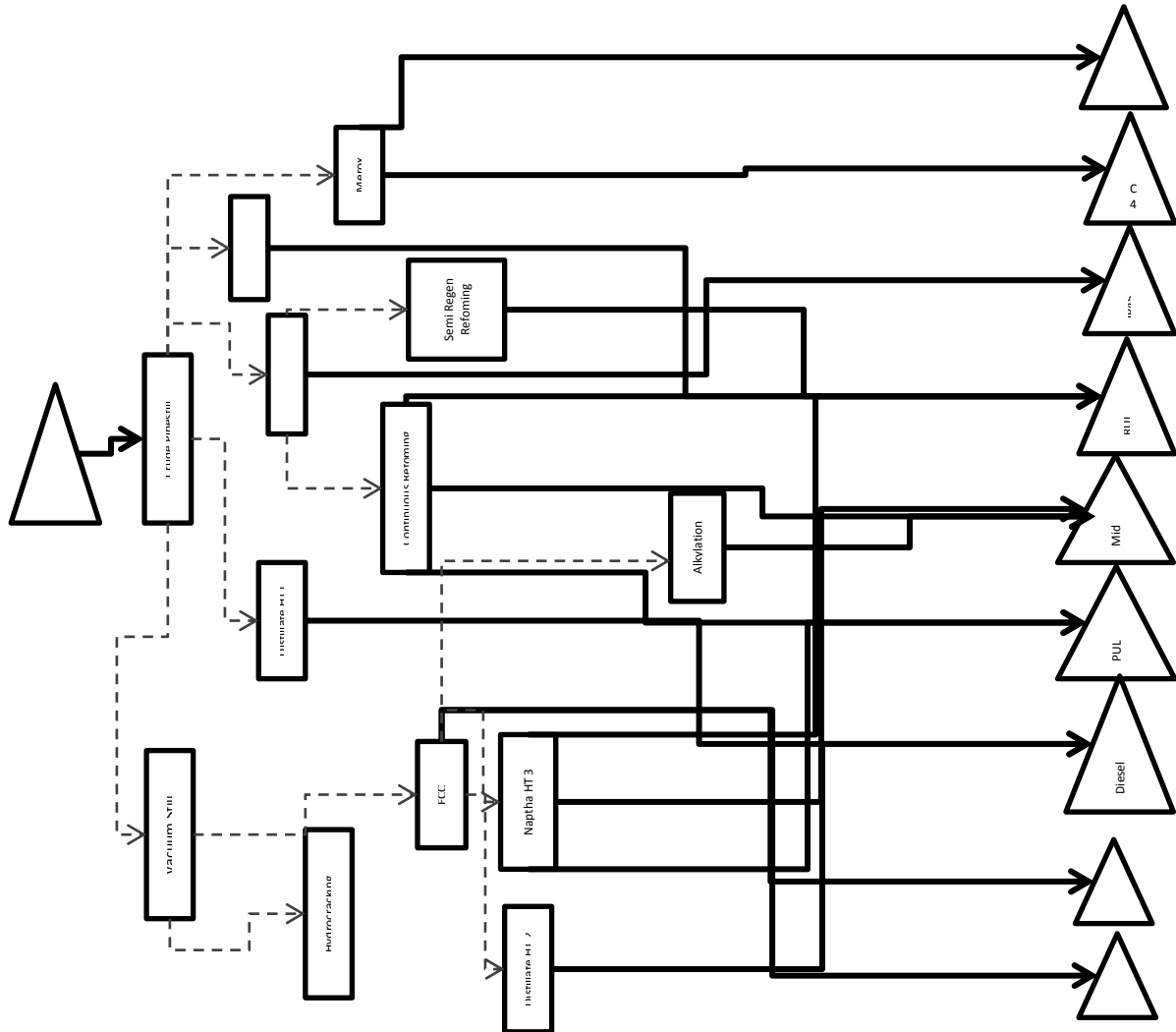


Figure 27: Case Study Refinery Lay-out

Table 1: Refinery Effluent to be Studied

Solid waste	Waste water	Air emissions
Crude oil sludges	Sour water	Sox
FCC spent Catalyst	Desalter Brine	NOx
Hydro processing Catalyst	Alky Spent Caustic	CO2
Desalter Micro Solids	Sewer run-offs	Particulate
		H2SO4
		VOCs

In this case study, wastes generated by the refinery is depicted in Table 1. Crude oil sludges are generated by the interaction of different types of crude oil in the storage tanks. The FCC and Hydroprocessing units account for all of the spent catalysts generated by the refinery. The amount of catalyst generated for disposal is influenced by the decline in activity due to poisoning or fouling. Desalters recovery of fine particulates in the crude oil account for the micro solids generated for disposal.

The largest fraction of waste water generated by the refinery is sour water formed from stripping sulfur laden crude. Crude distillation unit and the FCC are the two main contributors to sour water generation in this refinery. Other sources of waste water include Desalter Brine, Alky Spent Caustic and Oily water generated from Sewer run-offs. All waste water generated by the refinery is treated prior to disposal.

Air emission pollutants studied are described in Table 1. The FCC is the principal source for SO_x, NO_x and Particulates. SO_x and NO_x emissions are generated in the regeneration process of the catalyst. Particulates losses to the environment are generally a function of FCC cyclone efficiency and catalyst attrition. SO_x and NO_x are also generated to a lesser extent in the refinery furnaces and boilers along with CO₂ and H₂SO₄.

Table 2 illustrates the production capacity of the process units in the refinery. The Refinery is capable of an overall crude oil processing rate of 225000 tons per year. The combination of Continuous Reforming and a Semi Regen Reforming meet both the required high demand for high Octane components for gasoline blending and hydrogen needed by all the Hydrofining and Hydrocracking units. The FCC in this refinery process both native gas oils from the refinery Crude Distillation Unit and purchased virgin gas oils.

Table 2: Refinery Process Units and Production Limits

Process Unit	Upper Production limit (1000 ton/yr)
Crude Distillation Unit	225000
Continoust Rerforming Unit	25000
Semi Regen Reforming Unit	17000
Fluid Catalytic Cracking Unit	32000
Hydrocraking Unit	20000
Merox Treating Unit	7000
Distillate Hydrofining Unit 1	10000
Distillate Hydrofining Unit 2	5000
Naptha Hydrofining Unit 1	12000
Naptha Hydrofining Unit 2	8000
Naptha Hydrofining Unit 3	5000
Alkylation Unit	3000

The refinery has access to light and heavy crude oils as well as sour and sweet crude oils. Typically the decision on type and volume of crudes to process is based on economic considerations. Historically, the less processing or refining a crude oil must undergo the more valuable it is considered by the refinery (Parkash, 2003). Price differential between crude oils typically reflects the ease of refining. The refinery LP models has always preferred purchasing the ‘cheaper’ crude oils to achieve target production volumes based on regional market demand for final products (Famim et al, 2009).

The sulfur distribution of the different types of crude oil processed in the refinery is depicted in Figure 28. There is a wide range of options of crude oil available to the

refinery. They range from relatively simple processing of synthetic crudes (which contain little sulfur in the parts per million range) to heavy crudes which contain sulfur in the percentage levels.

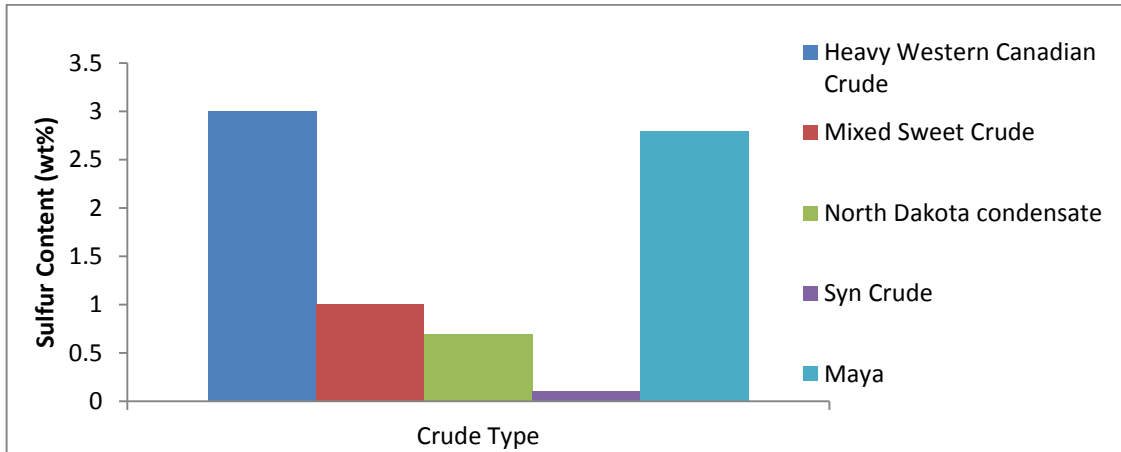


Figure 28: Refinery Crude Oil Option Sulfur Distribution

Similar to the sulfur, the crudes available to the refinery have a wide range of distribution of organic nitrogen. The relative nitrogen content generally follows the distribution of sulfur. Crudes that have high sulfur content generally will have high nitrogen content. Specifically, heavy crudes have been shown to have a higher fraction of both sulfur and organic nitrogen content.

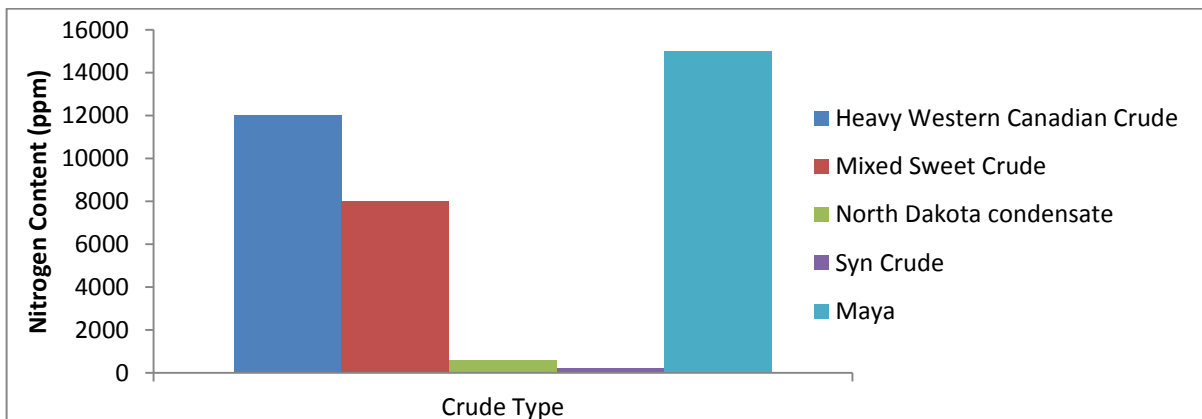


Figure 29: Refinery Crude Oil Option Organic Nitrogen Distribution

The following table illustrates the crudes available to the refinery. We show the properties that impact emissions and effluent waste from the refinery as well as respective cost of each crude.

Figure 30: Properties of Crudes Available to the Refinery

Crude Type	Sulfur Content (wt%)	Nitrogen Content (ppm)	Solids Content (BS&W)%	Max limit	Crude Cost (% of par)
Heavy Western Canadian Crude	3	12000	1.7	45%	0.78
Mixed Sweet Crude	1	8000	0.2	80%	1.02
North Dakota condensate	0.7	600	0.2	29%	1.12
Syn Crude	0.1	200	0.05	80%	1.3
Maya	2.8	15000	0.9	37%	0.95

The max limit column refers the maximum fraction of each crude that can be processed at any given time. Limitation on the amount of crude is primarily based on compatibility and fouling related issues with specific type of crude oil. Experience with operating above the given ranges have shown unwanted stable water emulsions in the desalter, foul preheat exchangers, and/or coke up pipestill furnace tubes (Wauquire, 2000). When this happens, the refinery has lost more than the advantage of purchasing the crude (Famim et al, 2009). Blending incompatible crude oils in the wrong proportions or even the wrong order, they can precipitate asphaltenes (called incompatibility). Once precipitated, it is difficult to redissolve asphaltenes quickly (Famim et al, 2009). Meanwhile, precipitated asphaltenes can cause stable oil-water emulsions, fouling of heat exchangers, and catastrophic coking of distillation furnace tubes (Wauquire, 2000).

6.2 Base Model output

The base model was run with emission caps and with no required emission mitigation requirements. As such, the model solved to maximize the profit of the refinery as defined by the objective function. In this section, we will show the solution chosen by the model based on the given constraints.

The following figure shows the model output for the base case optimum crude mix for the refinery. Not surprisingly, the model has chosen to maximize the least priced crudes of Maya and Western Canadian Heavy up to the maximum limit. It then chose to obtain the incremental crude by higher cost crudes of Mixed sweet blend and North Dakota condensate. Interestingly, it chose not to purchase Synthetic crudes since it is priced higher than the rest of the crudes. The cost of crude oil has the larger influence on refining business; it involves 80%–90% of the total product cost (Wauquiere, 2000).

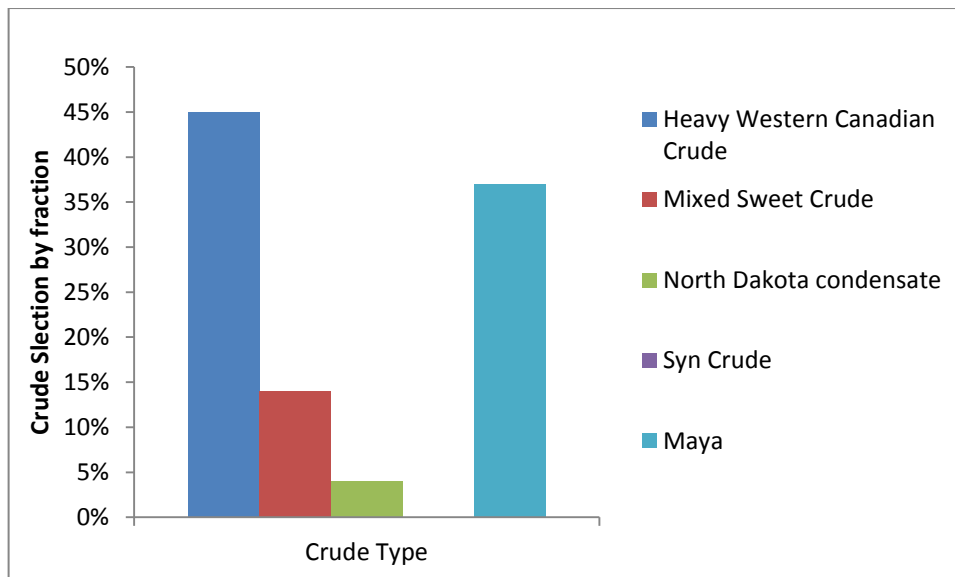


Figure 31: Base Case Model Output - Crude Selection by Type

Discounted crude oils, however, require additional processing to meet critical product specifications. Regardless of the inferiority placed upon the raw material, the model seems to suggest that it is always more profitable to process the lowest cost crude and chose to upgrade the midstreams in the refinery to produce the required final product qualities. The selected crude mix presents two disadvantages to the refinery.

The first disadvantage is the reduction in the yield of the straight run naphtha and distillate molecules and in increase in the VGO and vacuum residuum fraction. In general it is seen that the lower the API (the heavy the crude oil) the higher the impurities content and the lower the middle distillates yield (Jones & Pujadó, 2006). This reduction in the straight run material presents a challenge to the refinery to meet its product requirements. As such, we observe a very high load on the downstream upgrading units that produce naphtha and distillate molecules.

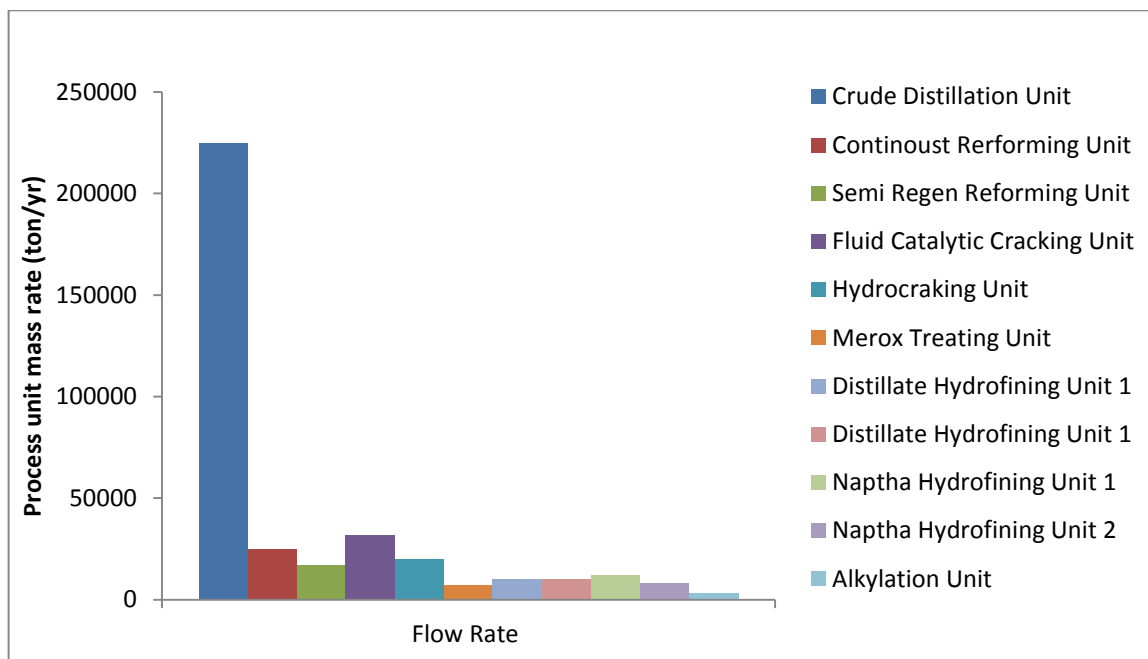
The second disadvantage is an increase in midstream upgrading occurs at the hydrotreaters due the impurities. Heavy petroleum is constituted by heavy hydrocarbons, and several metals (Riazi, 2005). In other words, we need to remove the impurities this means increased operating costs for the refinery. We require increase severity in the hydrotreaters which would put demand on the hydrogen generating facility in the refinery. The increased complexity in processing heavier and sourer crudes is very much outweighed by the per barrel cost savings the refinery sees on its raw material cost.

The properties of the base case mixed crudes can be shown in the following table.

Table 3: Base Case Model Output - Crude Slection Properties

Total Crude Properties	Sulfur Content (wt%)	Nitrogen Content (ppm)	Solids Content (BS&W)%
Refinery Crude Mix Base Case	2.554	12070.03	1.154

Figure 32 shows mass rates for each process units. It is interesting to observe the optimized base case shows the refinery is running to its maximum capacity rate based on the pipestill. The higher rates are driven by two reasons. One, the lower raw material cost lends its self to make the next barrel economics of the refinery to be highly profitable. As such, the optimized case would push the rates to maximum. Second, the lower yields of the naphtha and distillate molecules and increase in the vacuum residuum fraction, causes the model to require for maximum unit throughput in order to achieve the target finished product rates.

**Figure 32: Base Case Model Output - Process Flow Rates**

6.2.1 Solid Waste Sub Model Results and Analysis

The solid waste generated in the base case as defined earlier is achieved with no mitigation requirements placed on the model nor a cap on the total waste generated. It is interesting to note the more than 90% of the total oily sludge generated in the base case is generated in the pipestill. This might be an indication or an affirmation that in the base case, the optimum which is on a purely profit generating basis, the crude mix is not very compatible. We will use this as a basis for comparison in the subsequent cases to see if the total amount and the relative fraction of oil sludge generation in the pipestill changes.

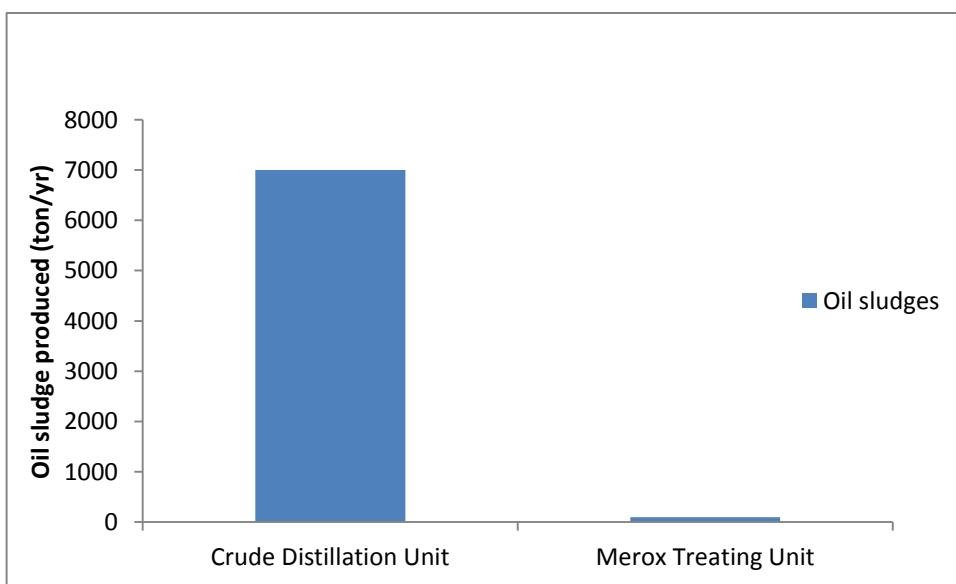


Figure 33: Base Case Model Output - Oil Sludge Production by Process Units

The vast majority of spent catalyst generated in the refinery is FCC catalyst. The rate at which the FCC spent catalyst is generated by is impacted by two factors. Primary factor is feed contaminants. If the feed being processed contains contaminants that have the effect of permanently deactivating the catalyst, then the purge rate of spent catalyst is increased. This is done in order to maintain equilibrium catalyst activity constant. Also,

with heavy crude processing the gas oils and residuum contain both higher amounts of basic and non-basic nitrogen compounds.

Basic nitrogen compounds are the type mainly responsible for poisoning FCC catalysts because poisoning occurs by the reaction of the basic nitrogen species with acid sites on the catalyst (Magee & Mitchell, 1993). The neutralization of catalytically active acid sites results in the deactivation of the catalyst. Nitrogen poisons also adversely affect selectivity (Sadeghbeigi, 2000). In addition, nitrogen in the feed is associated with asphaltenes and other coke precursors which contribute to catalyst poisoning (Magee & Mitchell, 1993). Other contaminants such as nickel act as a dehydrogenation catalyst which contributes to coke and gas production.

The second factor impacting FCC spent catalyst generation is increased FCC process rate. Increased rate typically has the effect of shortening the life span of each catalyst particle because of increase mass rate of contaminants and foulents being processed at each given period of time. Figure 34 shows the relative proportion of spent catalyst generation in the refinery as measured by the base case.

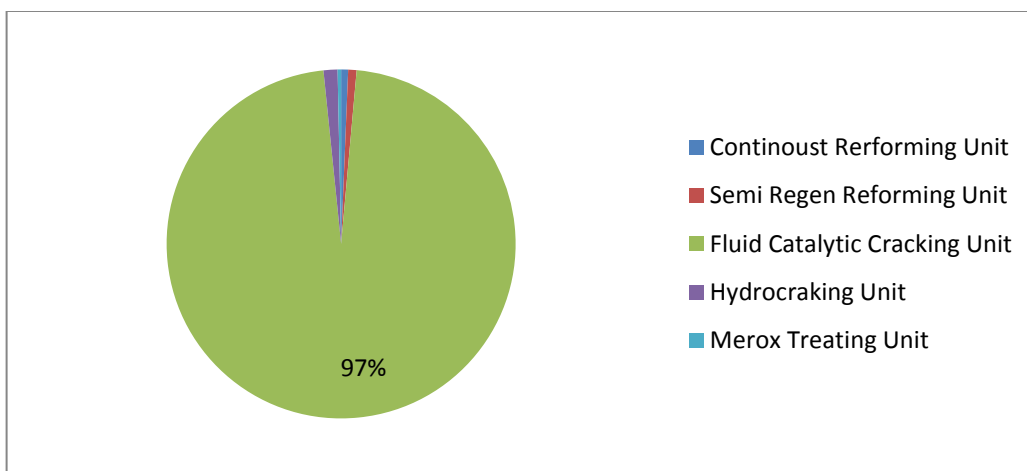


Figure 34: Base Case Model Output - Spent Catalyst Production by Process Units

Similar to the FCC catalyst, a substantial amount of the refinery waste generated can be attributed to process rate and the amount of treatment required by the hydrocarbon feed to the refinery in order to meet product quality guidelines. With increased heavy crude, we expect an increase in compounds such as sulfur, nitrogen, aromatics, iron, and other undesirable components. These compounds pose significant problems with catalyst poisoning.

For a numerical appreciation of the amount and distribution of solid waste generated as part of the base case solution, Table 4 is provided below.

Table 4: Base Case Model Output - Process Unit Solid Waste Generation

Process Unit	Flow Rate	Oil sludges	spent Catalyst	Hydro processing Catalyst	Desalter Micro Solids
Crude Distillation Unit	225000	7000			800
Continoust Rerforming Unit	25000		100	900	
Semi Regen Reforming Unit	17000		120		
Fluid Catalytic Cracking Unit	32000		15000		
Hydrocraking Unit	20000		200		
Merox Treating Unit	7000	100	50		
Distillate Hydrofining Unit 1	10000			700	
Distillate Hydrofining Unit 2	5000			50	
Naptha Hydrofining Unit 1	12000			80	
Naptha Hydrofining Unit 2	8000			120	
Naptha Hydrofining Unit 3	5000			200	
Alkyltion Unit	3000				

6.2.2 Wastewater Sub Model Output and Analysis

Sour water generated in the base case model is shown in Figure 35. Primary process units that generated most of the sour water in the refinery are the pipestill, hydrocracker and the fluid catalytic cracking unit. The sour water generated in refineries comes from numerous sources. Most refinery sour water systems contain some CO₂ and very high levels of H₂S. The potentially high H₂S content can make sour water extremely foul, and H₂S removal from the sour water to quite low levels is mandatory to avoid unacceptable pollution levels. As a result of the chosen crude slate, we expect to see relatively higher load of sour water to be generated in the refinery in the base case.

Deeper level of hydroprocessing can also lead to increased sour water generation.

Increased sulfur loading can quickly lead increased H₂S and ammonia loading in the cold separator section of the hydrotreatment units (Froment et al, 1999). In order to meet the metallurgical requirements for sulfur and ammonia balance, one would need to increase the amount of fresh water used as a supplemental wash (Froment et al, 1999).

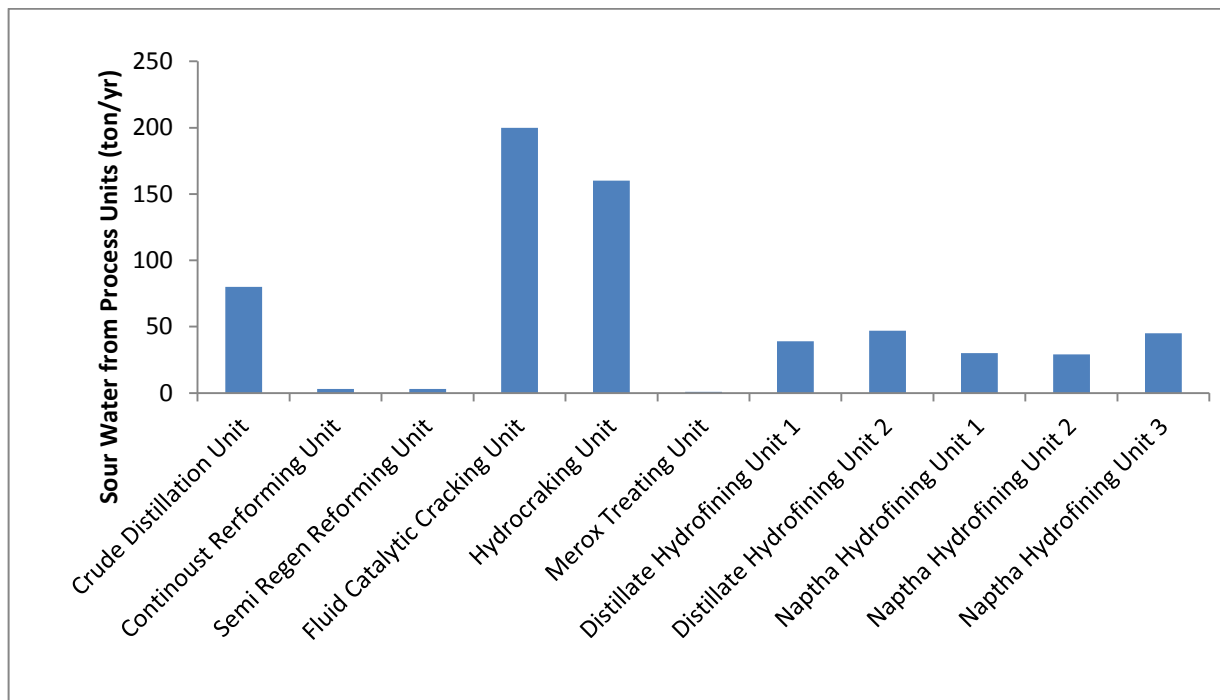


Figure 35: Base Case Model Output - Sour Water Production by Process Units

With heavier crude processing, there much more demand placed on the desalting operation due to increased load of salts and other inorganic minerals in the raw crude. Desalter operating temperatures can decrease by 30° to 40° F., if no additional surface area is added to the cold exchanger train (Jones & Pujadó, 2006). The desalted crude's salt content can increase dramatically if the temperature is too low (Wauquire, 2000). Many heavy crudes Maya can have high salt contents depending on production field operations; therefore, good desalter performance is critical. Poor cold exchanger train

designs often cause low desalter temperatures, poor salt removal, and periodic upsets that send large quantities of brine to the waste water treatment plants (Jones & Pujadó, 2006).

The optimized base case show the refinery generating spent caustic from scrubbing liquor from a variety of sources including gasoline sweetening, gasoline and LPG prewashing, gasoline and LPG mercaptan extraction, and olefin cracked gas scrubbing. Caustic washing aids in the refining process and improves product quality by removing sulfidic and acid components. It is expected that the generation rate to be proportional to the amount of sulfur in the feed.

Figure 36: Base Case Model Output - Wastewater Production by Process Units

Process Unit	Flow Rate	Sour waster	Desalter Brine	Alky Spent Caustic	Sewer run-offs
Crude Distillation Unit	225000	80	1200	80	29
Continoust Rerforming Unit	25000	3			33
Semi Regen Reforming Unit	17000	3			20
Fluid Catalytic Cracking Unit	32000	200		50	23
Hydrocraking Unit	20000	160			56
Merox Treating Unit	7000	1		250	90
Distillate Hydrofining Unit 1	10000	39			9
Distillate Hydrofining Unit 2	5000	47			36
Naptha Hydrofining Unit 1	12000	30			25
Naptha Hydrofining Unit 2	8000	29			10
Naptha Hydrofining Unit 3	5000	45			5
Alkylation Unit	3000			700	13

6.2.3 Air Emission Sub Model Output and Analysis

The Air emissions generated in the base case model is shown in Table 5. CO₂ generation, which is shown in the fifth column, can be shown to be proportional to the carbon/hydrogen ratio of a crude fraction or the extent to which these fractions can be converted to lighter components in the Conversion processes. The lighter the crude is, the lighter the energy (fuel) used in crude distillation (Jones & Pujadó, 2006). Synthetic crude oil for example contains essentially no vacuum residuum thereby essentially eliminating a fraction of fuel that would have been consumed in the vacuum heater. The heavier the crude oil the higher the volumetric yields of vacuum gas oil and residuum fractions, the higher the through-put and/or the operating severity in the conversion units (FCC and hydrocracking) needed to produce a given product slate, and hence the higher the refinery energy consumption (Antos & Aitani, 2004).

CO₂ emissions from a refinery are primarily a consequence of refinery energy use. The volumetric yields and properties of a crude oil's fractions affect refinery energy use. This is due the extent of processing requirements needed in various process units to meet product volume and quality requirements.

The sources of energy used in this refinery are fuel gas containing molecules ranging from methane to propylene (Parkash, 2003). This makes the gas more carbon intensive than natural gas which is available for purchase (Jones & Pujadó, 2006). Refineries that rely most on the more-carbon-intensive sources will tend to have higher CO₂ emissions per barrel of crude throughput than refineries that rely more on less-carbon-intensive sources.

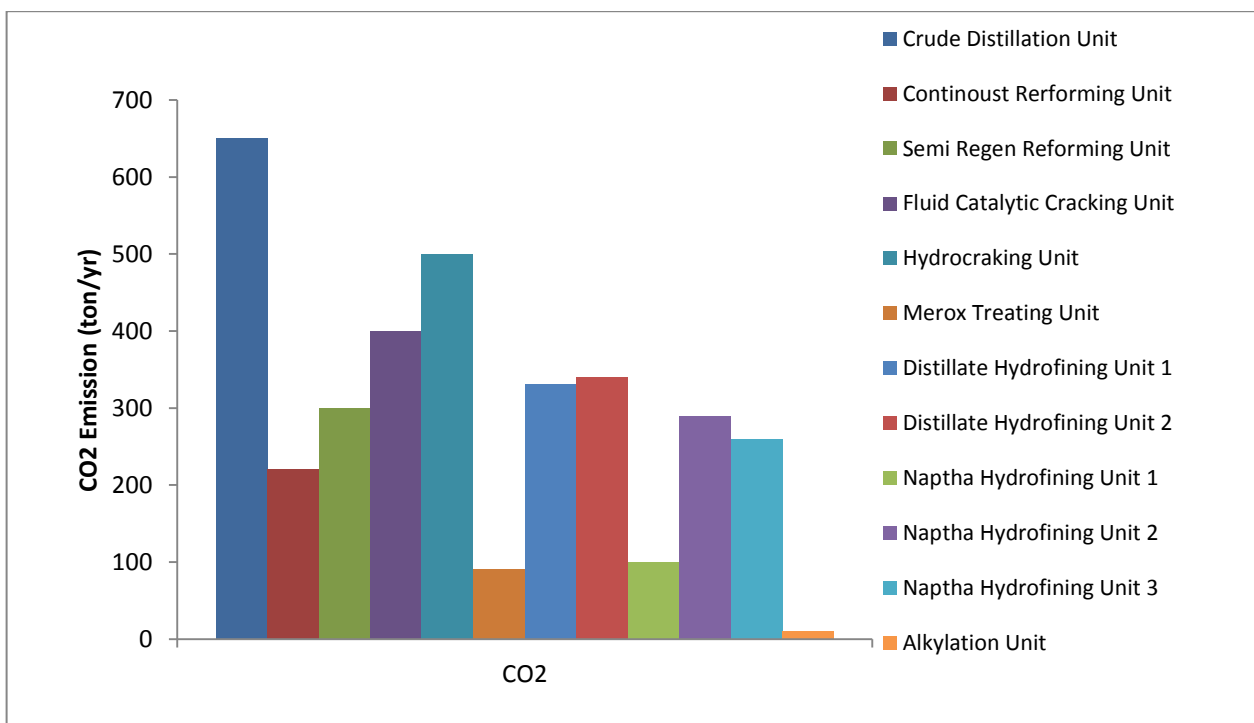


Figure 37: Base Case Model Output - CO2 Emissions by Process Units

The FCC accounts for the largest producer of SO₂ emissions in the base case. The amount of SO₂ emitted from a FCC regenerator is a function of the quantity of sulfur in the feed, coke yield, and conversion. Generally, 45% to 55% of feed sulfur is converted to H₂S in the FCC reactor, 35% to 45% remains in the liquid products, and about 5 - 10% is deposited on the catalyst in the coke (Bhattacharyya et al, 1999). It is this sulfur in the coke which is oxidized to SO₂ (90%) and SO₃ (10%) in the FCC regenerator (Bhattacharyya et al, 1999).

Much of the fuel required by refinery process heaters and boilers is produced by the refinery itself (Parkash, 2003). Most of the SO₂ emissions from refinery combustion sources result from the use of liquid fuels such as low distillates which could have sulfur range in the 1 wt% range (Bhattacharyya et al, 1999). Because of their relatively high

sulfur concentrations, these fuels are frequently unsuitable for marketing. Combustion of refinery gases also results in SO₂ emissions; however, these gases are generally scrubbed for removal of sulfur values prior to burning and thus produce relatively little SO₂ in comparison with residual fuel oil combustion (Bhattacharyya et al, 1999). SO₂ production is being aggravated by the fact that refinery is processing heavy crude as part of its feed mix. It is reasonable to assume that if the overall feed sulfur was lower, SO₂ generated by the process units would be less than the base case. As always this would come at a cost to the refinery as it increases its overall cost of operation.

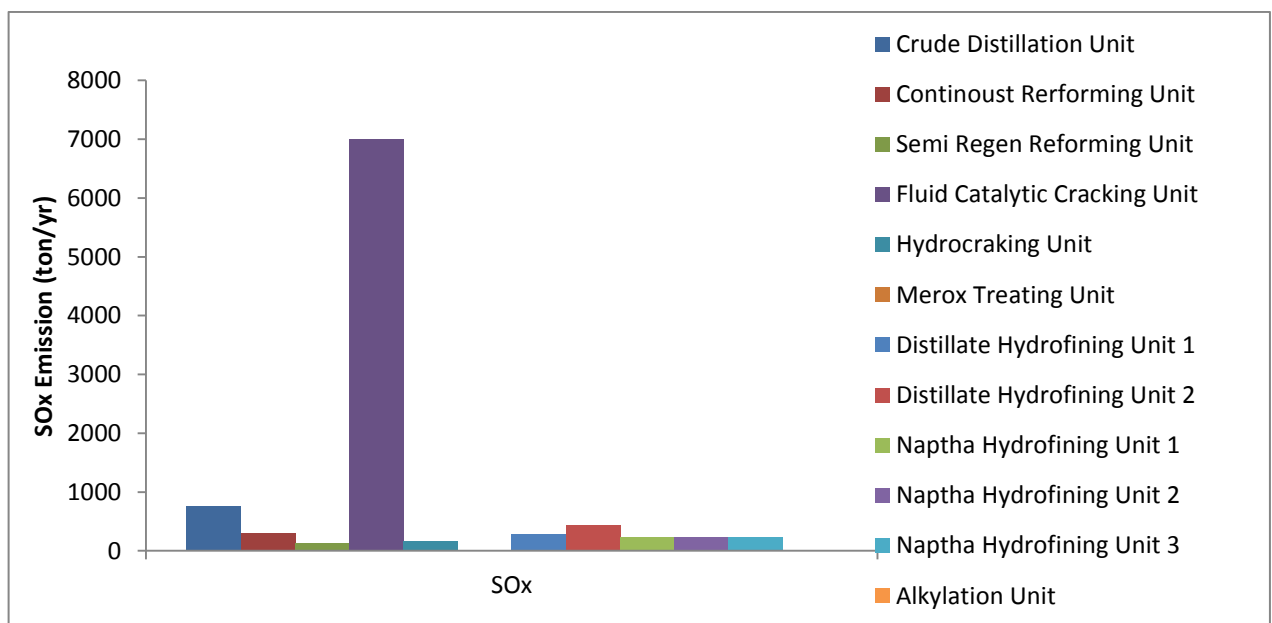


Figure 38: Base Case Model Output - SO_x Production by Process Units

The base case data for the air emission generation is shown in Table 5. The Crude Distillation Unit provides a nominal amount of SO_x, NO_x and CO₂ though the process heaters. The FCC remains in the base case as the primary source of all air emission through the catalyst regeneration process. Both reforming units are a relatively high

source of CO₂ through process inter-heaters which fire refinery fuel gas with relatively high amounts of hydrogen gas.

Table 5: Base Case Model Output - Air Emission by Process Units

Process Unit	Flow Rate	SO_x	NO_x	CO₂	Particulate	H₂SO₄
Crude Distillation Unit	225000	750	120	650		10
Continoust Rerforming Unit	25000	300	30	220		22
Semi Regen Reforming Unit	17000	140	10	300		21
Fluid Catalytic Cracking Unit	32000	7000	150	400	600	440
Hydrocraking Unit	20000	160	17	500		50
Merox Treating Unit	7000		23	90		9
Distillate Hydrofining Unit 1	10000	290	20	330		90
Distillate Hydrofining Unit 2	5000	440	10	340		30
Naptha Hydrofining Unit 1	12000	230	32	100		20
Naptha Hydrofining Unit 2	8000	229	21	290		10
Naptha Hydrofining Unit 3	5000	233	9	260		50
Alkylation Unit	3000			10		13

6.3 Constraining Solid Waste Generation

In the solid waste sub model optimization, solid waste generation will be reduced by streamlining crude processing at the refinery in order to reduce sludge make at the CDU (*feed switch*). This can be achieved but has the consequences of increasing the logistics and scheduling at the refinery. Streamlining crude processing attempts to reduce the

incompatibility of the crudes being processed and ultimately reduce the asphaltene precipitations caused by incompatible crudes.

The resultant, although a 2% reduction in sludge make was observed, the increased logistics had an upward impact on the refinery operating cost by 4%. The increased cost is primarily due to the costs required to meet the logistics limit in the refinery and thereby not always purchasing the most economic crudes. This is a rather big shift in the operating cost to only achieve a relatively small reduction in solids sludge generation from the pipestill.

Table 6: Solid Waste Constrained Model - Crude Distillation Unit Process Rate

Process Unit	Flow Rate	Oil sludges Reduction	Desalter Micro Solids Reduction
Crude Distillation Unit	225000	2%	1%

Table 7: Solid Waste Constrained Model - Crude Distillation Unit Processing Cost Impact

Process Unit	Flow Rate	Oil sludges Reduction	Desalter Micro Solids Reduction
Crude Distillation Unit	225000	4%	0.8%

The sub model total crude sulfur limit constraint was reduced from an average of 2.5 wt% to 1.5 wt%. This allowed for a reduction in the intermediate stream sulfur content which then reduced the loading on the hydroprocessing and the FCC units. Therefore reducing the interval of catalyst change-outs and ultimately leading to reducing the amortized annualized weight of catalyst sent to landfills. The output of this case is shown in the following table. The impact on the overall refinery operating cost is shown in Table 8.

Table 8: Solid Waste Constrained Model - Hydroprocessing Catalyst Reduction

Process Unit	Flow Rate	Hydro processing Catalyst Reduction
Crude Distillation Unit	225000	
Continoust Rerforming Unit	25000	
Semi Regen Reforming Unit	17000	
Fluid Catalytic Cracking Unit	32000	
Hydrocraking Unit	20000	
Merox Treating Unit	7000	
Distillate Hydrofining Unit 1	10000	4%
Distillate Hydrofining Unit 2	5000	2%
Naptha Hydrofining Unit 1	12000	3%
Naptha Hydrofining Unit 2	8000	2%
Naptha Hydrofining Unit 3	5000	2%
Alkylation Unit	3000	

Interestingly, the optimized model output did not include a capture technology such as landfill in order to meet the effluent reduction. Instead, there was a piecemeal effort of increased logistics cost of choosing compatible crudes for sludge reduction and valuing crudes on base contaminant basis as a way of meeting effluent targets. This was primarily due to the large initial capital costs and the continuing operating cost of the capture technology.

Table 9: Solid Waste Constrained Model - Capture Technology Profile

Approach	effluent reduction	change in operating cost	Capital Cost Required
Capture Technology	62%	19%	\$ 2,300.00

Constraining the overall sulfur in the refinery generates crude switches. The Maya crude fraction in the overall crude mix to refinery in the base case was optimized at its max limit of 37% and the western Canadian crude content in the base was also at its max content of 45%. In the constrained case, the Maya content is reduced to 19% while the western Canadian crude is reduced to 10% of the overall crude mix to the refinery.

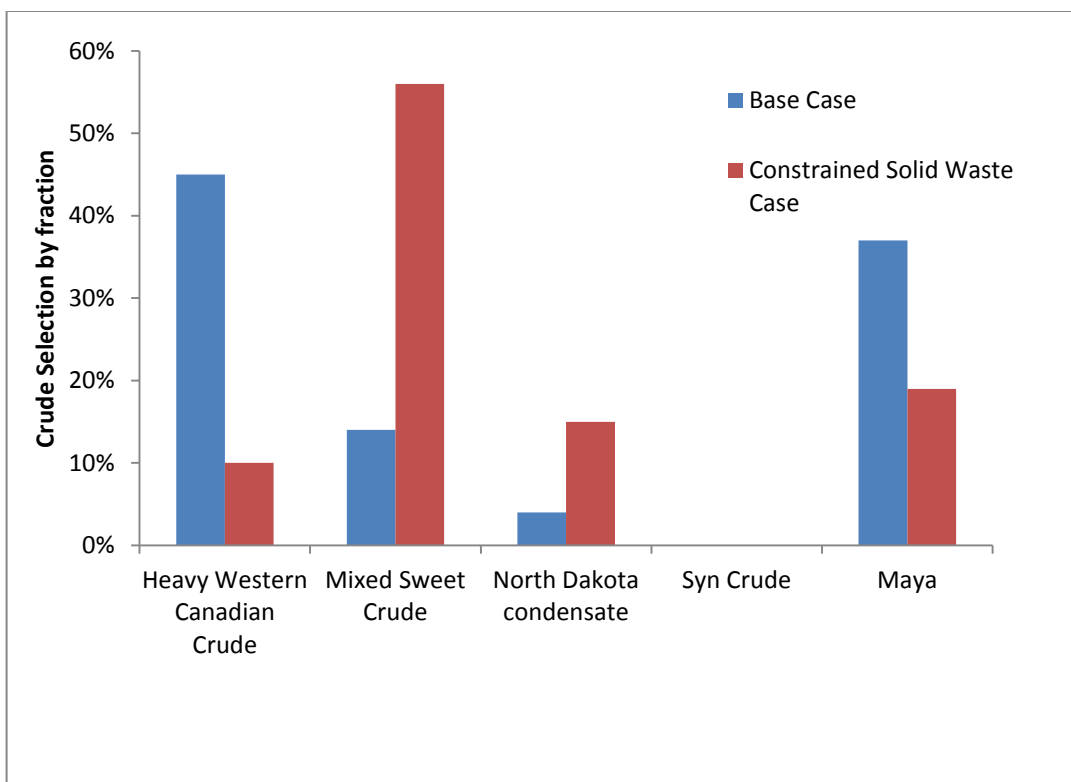


Figure 39: Solid Waste Constrained Model - Optimized Crude Selection by Type

Sulfur as a poison impairs refinery catalyst performance by reducing catalyst activity via competitive adsorption onto the active sites or by alloy formation with the active sites and the result is to effectively remove these active centres from the desired reaction scheme (Wauquire, 2000). Poisoning by a chemisorptions mechanism is directly due to the fact that the poison is more strongly absorbed than a reactant. Reducing the overall crude sulfur as determined by the optimized constrained case shows the following reductions:

Table 10: Solid Waste Constrained Model - Solid Waste Reduction in Optimized Case

Process Unit	Flow Rate	spent Catalyst Reduction	Hydro processing Catalyst Reduction
Crude Distillation Unit	225000		
Continoust Reforming Unit	25000	4%	
Semi Regen Reforming Unit	17000	2%	
Fluid Catalytic Cracking Unit	32000	1%	
Hydrocraking Unit	20000	9%	
Merox Treating Unit	7000	21%	
Distillate Hydrofining Unit 1	10000		5%
Distillate Hydrofining Unit 2	5000		4%
Naptha Hydrofining Unit 1	12000		5%
Naptha Hydrofining Unit 2	8000		4%
Naptha Hydrofining Unit 3	5000		4%
Alkylation Unit	3000		

There are several conclusions that can be made from the output of the constrained model case. The most interesting of all conclusions is that the cost of emission reduction did not justify building a new capture technology in order to achieve the desired goals of reducing the effluent from the refinery. Rather, the model shows there is a better justification for incurring increased operating costs by not purchasing the more economic crudes and thereby achieve the targets by generating less emission precursors to intermediary process units and thereby achieve longer 'life' out of the process catalyst.

This is a strategic decision making and one that is not common in today's refineries.

Operating on a margin based business, it is has always been the norm to purchase the

most economic feeds and uplift these feeds to the most profitable products. This typically entails purchasing heavy sour crudes and increasing operating severity in the process unit to achieve the desired high margin products. Optimized constrained model seems to suggest, that in an environment in which solid waste is to be minimized, more of an effort needs to be placed on purchasing the ‘right’ crudes to achieve this goal.

6.4 Constraining Wastewater Production

In the Wastewater sub model, the initial attempt was to constrain the base model by creating a route for refinery spent caustic from the merox units to the wastewater treatment plant. In the base case, it was observed that the refinery was purchasing fresh caustic in order to control the pH of the oily water to the BIOX unit. The base wastewater from the refinery is slightly acidic and therefore caustic is purchased to maintain a slightly basic environment from the optimal operation of the biological unit. In essence, a small recycle loop is created within the refinery.

Allowing for this change in the refinery connectivity, a reduction is observed in the amount of caustic that is generated for disposal. The impact of allowing the spent caustic to be reprocessed within the refinery without any incremental capital expenditures is shown in the following:

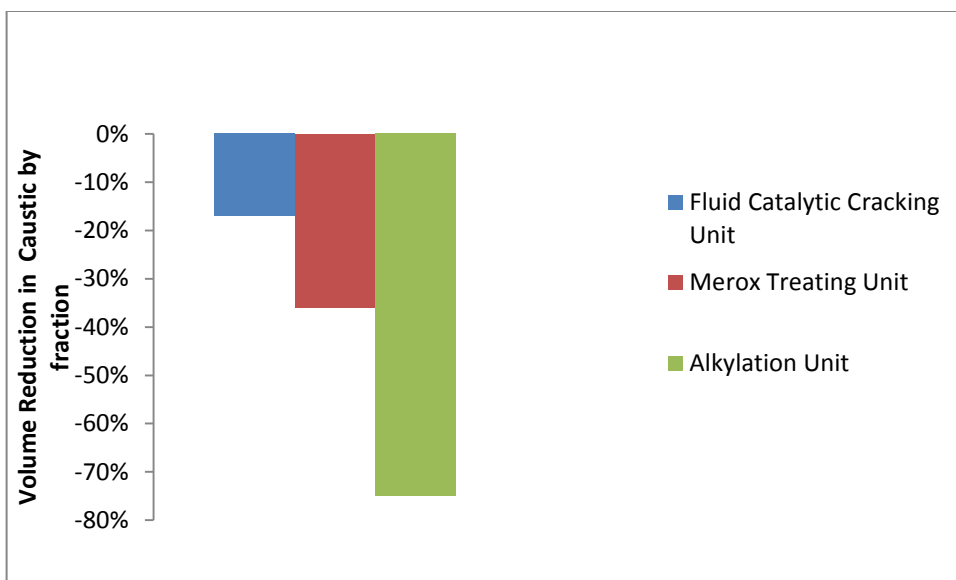


Figure 40: Wastewater Constrained Model - Volume Reduction in Alkylation Spent Caustic

The operating cost of each process unit impacted by this change is shown Figure 41:

Wastewater Constrained Model - Operating Cost Reduction Associated with Alkylation Spent Caustic. As expected, a reduction in the operating cost for each one of the process units involved in this new 'recycle' loop is observed.

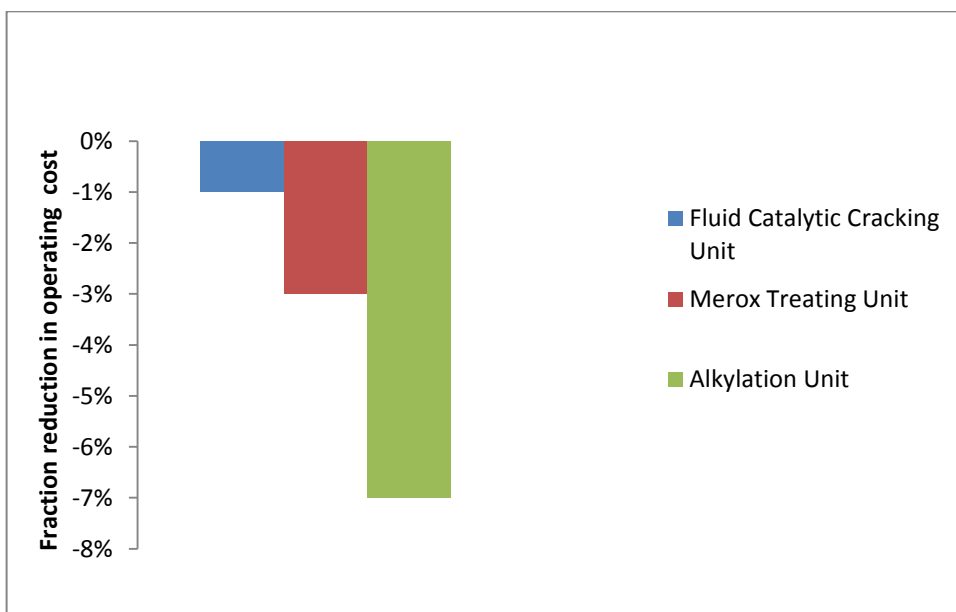


Figure 41: Wastewater Constrained Model - Operating Cost Reduction Associated with Alkylation Spent Caustic

In the next phase, an attempted is made to constrain the overall model feed sulfur limit by allowing the model to conduct crude switches at the pipestill. Unlike the solid waste model, there is a weaker relationship between overall waste water produced and the crude sulfur limit. As such, it is observed a larger step change in the sulfur limit in order to achieve the desired reduction in sour water production.

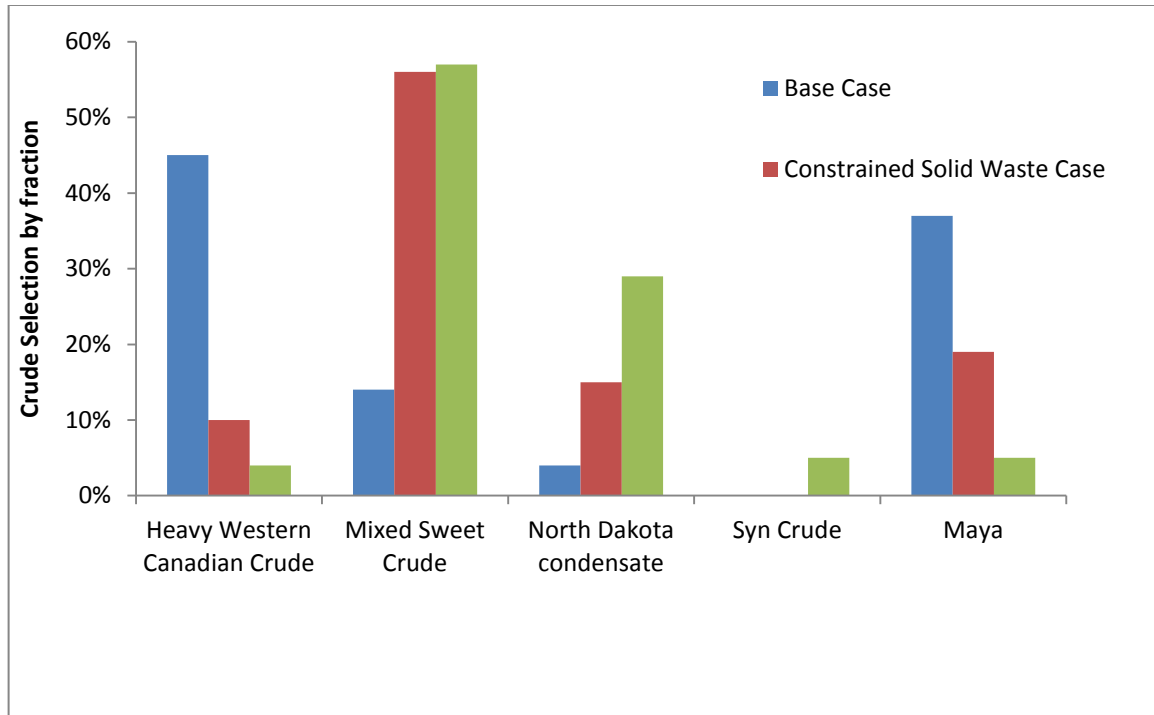


Figure 42: Wastewater Constrained Model - Crude Selection by Type in Caustic Reprocessing Case (Comparison with Base Case and Solid Waste Constrained Models)

The output of the case shows a large reduction in heavy fraction of the overall refinery feed. Interestingly, the case still has some of the more expensive synthetic crude in the mix. The crude selection by type is shown in

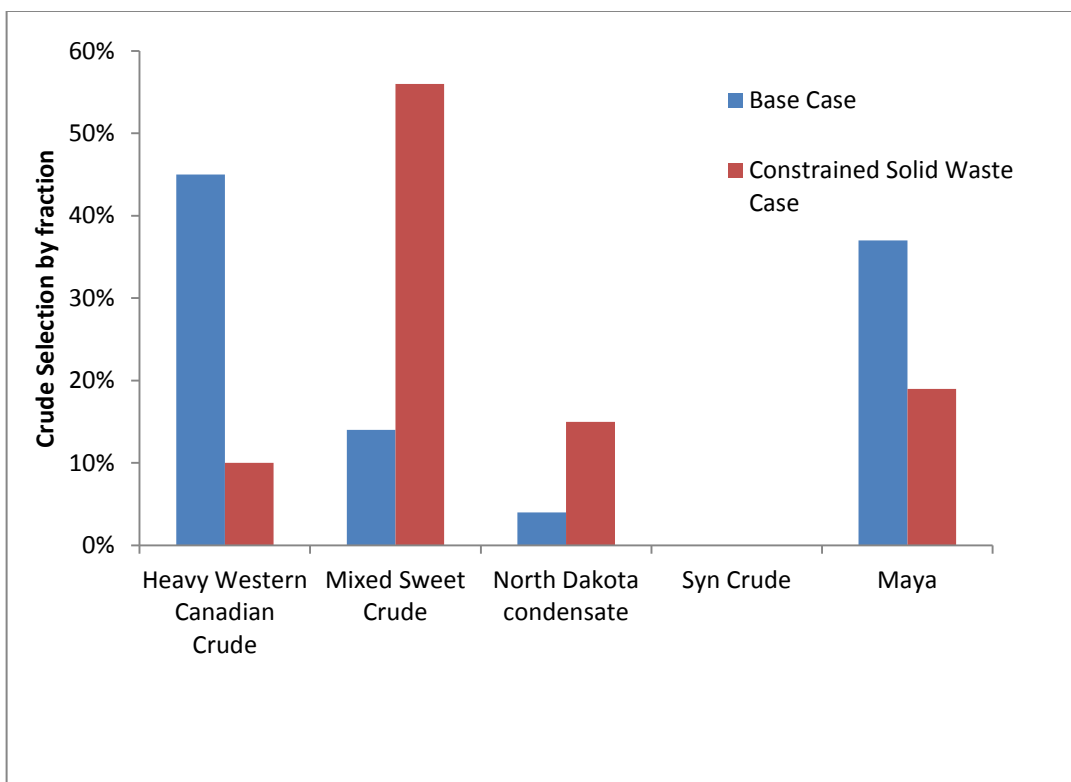


Figure 39. The overall average feed qualities in the optimized constrained case are shown in Table 11 below.

Table 11: Wastewater Constrained Model - Crude Selection Properties in Caustic Reprocessing Case

Total Crude Properties	Sulfur Content (wt%)	Nitrogen Content (ppm)	Solids Content (BS&W)%
Refinery Crude Mix Base Case	1.038	5800.203	0.4325

The optimal case shows relatively small decrease in the sour water make and caustic produced as the sulfur in the crude is reduced. The optimality shift from the base case model is shown in the following table:

Table 12: Wastewater Constrained Model –Wastewater Reduction in Caustic Reprocessing Case by Volume

Process Unit	Sour waster	Desalter Brine	Alky Spent Caustic
Crude Distillation Unit	1.2%	1.5%	0.9%
Continoust Rerforming Unit	0.2%		
Semi Regen Reforming Unit	0.2%		
Fluid Catalytic Cracking Unit	1.5%		1.0%
Hydrocraking Unit	0.3%		
Merox Treating Unit	0.0%		2.0%
Distillate Hydrofining Unit 1	0.2%		
Distillate Hydrofining Unit 2	0.4%		
Naptha Hydrofining Unit 1	0.1%		
Naptha Hydrofining Unit 2	0.3%		
Naptha Hydrofining Unit 3	0.2%		
Alkylation Unit			3.0%

The changes introduced as part of altering the crude slate from the base had an impact in reducing the overall cost to process sour water and other waste water streams in the refinery. The reduction in the operating cost is primarily associated with reduction in the overall waste water generation in each process. The operating cost impact of restricting the crude slate to the refinery is shown in the following table:

Table 13: Wastewater Constrained Model -Sour Water, Deslater Brine and Alkylation Spent Caustic Opeating Cost Reduction in Optimal Case

Process Unit	Sour waster	Desalter Brine	Alky Spent Caustic
Crude Distillation Unit	1.0%	1.1%	0.6%
Continoust Rerforming Unit	1.2%		
Semi Regen Reforming Unit	3.2%		
Fluid Catalytic Cracking Unit	2.6%		1.2%
Hydrocraking Unit	0.9%		
Merox Treating Unit	0.0%		1.1%
Distillate Hydrofining Unit 1	1.2%		
Distillate Hydrofining Unit 2	1.4%		
Naptha Hydrofining Unit 1	1.1%		
Naptha Hydrofining Unit 2	0.7%		
Naptha Hydrofining Unit 3	0.8%		
Alkylation Unit			2.1%

In the next phase, sour water is segregated into two different categories. The first is the high pH sour water with pH between 5.5 and 6.5. The second category is low pH sour water with pH below 5.5. The case is re-optimized for feed switch and with the added flexibility to re-process sour water within the refinery. The optimized feed slate sulfur content moves from the overly constrained case of 1 wt% to 1.2 wt%. The optimal crude slate shift is shown in the following table:

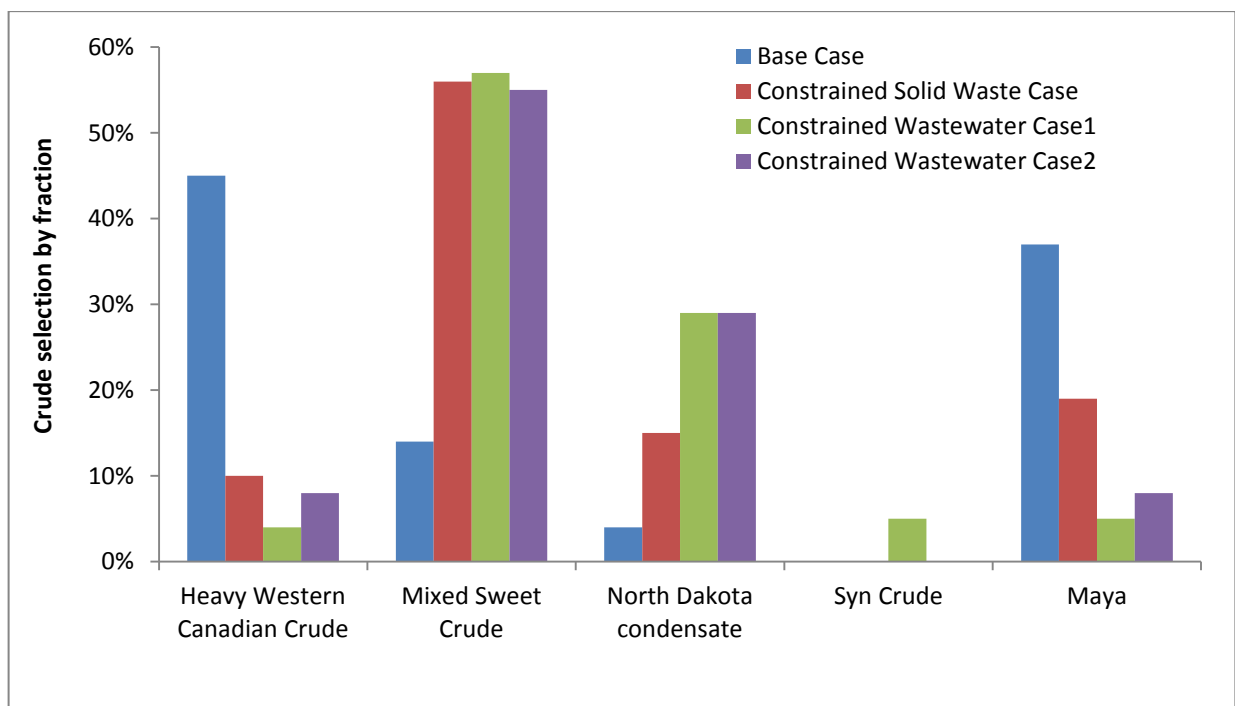


Table 14: Wastewater Constrained Model - Crude Selection by Type in Sour Water Segregation Case

Note the change in the heavy crude fraction in the model and the elimination of the synthetic crude from the crude slate. These changes allow for processing of a more cost effective crude mix in the refinery feed while meeting the required effluent reductions. As discussed in the base case, synthetic crudes are relatively costlier than the other crudes in the batch. The profile base contaminants into the refinery are show in the next table:

Table 15: Wastewater Constrained Model - Crude Selection Properties in Sour Water Segregation Case

Total Crude Properties	Sulfur Content (wt%)	Nitrogen Content (ppm)	Solids Content (BS&W)%
Refinery Crude Mix Base Case	1.217	6560.203	0.521

The optimized case output for the waste water generation is shown in following table. It is observed marginal reduction in sour water make due to the slight reduction in the overall refinery feed sulfur level. On the other hand, it is observed relatively large reduction in spent caustic discharged and desalter brine.

Table 16: Wastewater Constrained Model - Wastewater Reduction by Volume in Sour Water Segregation Case

Process Unit	Sour waster	Desalter Brine	Alky Spent Caustic
Crude Distillation Unit	0.8%	1.5%	0.9%
Continoust Rerforming Unit	0.1%		
Semi Regen Reforming Unit	0.1%		
Fluid Catalytic Cracking Unit	1.6%		1.0%
Hydrocraking Unit	0.4%		
Merox Treating Unit	0.0%		2.0%
Distillate Hydrofining Unit 1	0.2%		
Distillate Hydrofining Unit 2	0.4%		
Naptha Hydrofining Unit 1	0.1%		
Naptha Hydrofining Unit 2	0.3%		
Naptha Hydrofining Unit 3	0.2%		
Alkylation Unit			3.0%

The refinery operating cost reduction associated with optimized case is shown in the following table. We note the relatively large reductions associated with operating cost of treating sour water from both the FCC and the reforming units. Sour water from the FCC contains relatively higher amounts of sulfur than the other units in the refinery. Additionally, the optimized case did show large reduction in the actual mass of sour water generated from the FCC.

Table 17: Wastewater Constrained Model - Wastewater Processing Cost Reduction in Sour Water Segregation Case

Process Unit	Sour waster	Desalter Brine	Alky Spent Caustic
Crude Distillation Unit	0.7%	1.1%	0.6%
Continoust Rerforming Unit	1.1%		
Semi Regen Reforming Unit	3.1%		
Fluid Catalytic Cracking Unit	2.8%		1.2%
Hydrocraking Unit	0.9%		
Merox Treating Unit	0.0%		1.1%
Distillate Hydrofining Unit 1	1.2%		
Distillate Hydrofining Unit 2	1.4%		
Naptha Hydrofining Unit 1	1.1%		
Naptha Hydrofining Unit 2	0.7%		
Naptha Hydrofining Unit 3	0.8%		
Alkylation Unit			2.1%

6.5 Constraining Air Emission

In the air model, the option of converting the refinery fuel system from refinery fuel gas to natural gas is explored. Although containing less energy per unit of mass, the natural gas is much cleaner as it does not contain any sulfur or mercaptain compounds. The optimized model shows a reduction of emissions from the base case as shown in the next table:

Table 18: Air Emission Constrained Model - Optimized Case Air Emission

Process Unit	SO _x	NO _x	CO ₂	Particulate	H ₂ SO ₄
Crude Distillation Unit	4.0%	0.1%	12.0%		0.3%
Continoust Reforming Unit	2.0%	0.1%	18.0%		0.3%
Semi Regen Reforming Unit	3.0%	0.1%	17.0%		0.3%
Fluid Catalytic Cracking Unit	0.1%	0.1%	2.0%	0.0%	0.3%
Hydrocraking Unit	3.4%	0.1%	10.0%		0.3%
Merox Treating Unit	0.0%	0.1%	0.0%		0.3%
Distillate Hydrofining Unit 1	2.0%	0.1%	4.0%		0.3%
Distillate Hydrofining Unit 2	3.0%	0.1%	2.0%		0.3%
Naptha Hydrofining Unit 1	2.0%	0.1%	3.0%		0.3%
Naptha Hydrofining Unit 2	2.0%	0.1%	2.0%		0.3%
Naptha Hydrofining Unit 3	1.0%	0.1%	2.0%		0.3%
Alkylation Unit			0.0%		0.0%

The impact on the cost to operate the refinery is shown in the following table. We observe large reduction in all process units which are energy intensive. For example, the CDU, which in this refinery contains three large preheat furnaces and a vacuum furnace observes a reduction of 14% in the overall cost to treat the effluent gas. We see a similar reduction in both Reforming and Hydrofining units. Alternatively, we see lesser reduction in the FCC due to the heat integration of the unit making it low heat intensive process unit.

Table 19: Air Emission Constrained Model - Operating Cost Increase in Optimized Case

Process Unit	Cost increase
Crude Distillation Unit	14.0%
Continoust Rerforming Unit	22.0%
Semi Regen Reforming Unit	13.0%
Fluid Catalytic Cracking Unit	0.1%
Hydrocraking Unit	4.4%
Merox Treating Unit	0.0%
Distillate Hydrofining Unit 1	12.0%
Distillate Hydrofining Unit 2	23.0%
Naptha Hydrofining Unit 1	12.0%
Naptha Hydrofining Unit 2	12.0%
Naptha Hydrofining Unit 3	11.0%
Alkylation Unit	

7.0 Conclusion

Petroleum refining is an essential industrial process that provides the world refined hydrocarbon for power generation. This industrial system is also responsible for generating environmentally harmful compounds. In this thesis we have attempted to use system analysis tools to design a program that allows for the selection of the optimal control, minimize and treating options for petroleum refinery waste streams. The refinery model developed by Elkamel and Al-Qahtani (2007) was used. This model was supplemented with constraints on solid waste generation, waste water production, and effluent air emissions. The overall model was designed to determining the best method for minimizing the generation of emissions while recommending the optimal method of treating the waste.

The costs of treatment and environmental impacts of each pollutant is taken as inputs to the model. The model was tested on an existing refinery in North America. In most cases, the model selected options that reduced emission precursors in the crude oil by selecting the lightest and relatively 'cleanest' crude oil in to the refinery. In all cases, this increased the cost of crude but had the impact of reducing the overall emissions out of the refinery. The model that has been developed can help decision makers in the refining industry plan for the regulatory changes that are sure to come in the near future by considering options to reduce emission from their respective refineries. Capital expansions and new grass roots treating facilities are not always the answer. In the case study, slight changes in the feed and new flexibility within the facility can achieve the desired reduction in emissions.

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